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AUTHORS INDEX

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Vol. XXI, 1944

SUBJECT INDEX

ERRATA

Page.	Line.	*Read*	*for*
22	Fig. 5	Ascorbic acid= $2\times10^{-2}M$	Ascorbic acid= $1\times10^{-2}M$
25	3	26.7×10^{-4} mg of Cd	26.7×10^{-4}mg
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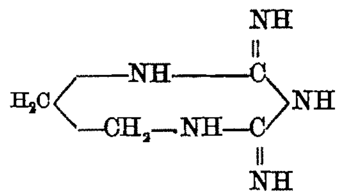
	below 12	*Read* Ditter's formula as 	
88	12*	asymmetrical	symmetrical
133	1*	*Dec.* 21, 1943	Dec. 21, 1944
157	2	filter S 53	filter 533
158	Below Fig 2	After ½—¾ hr	After 1—¾ hr
187	4	p_H 5.1 to 5.33	p_H 5.2 to 5.3
187	23	1 $Bi^{\cdots}\equiv$ 1 As^{5+}	1 Bi≡1 As
187	26 Table column 3	I_2 soln. (0.999N/10)	I_2 soln. (0.999N)
189	Table 1	*Read* the figures of the last line (of Group I) as of Group II (in presence of Am. acetate)	
190	Table II, column 6	1.196 mg.	1.106 mg.
194	16*	(D. R. C.)	(D. R. C. 111)
196	Table IIA, line 1	results	recone'ts
197	,, line 1	*Insert* "with" before "10 c.c of latex"	
198	5	Table IIC	Table IIB
	6	(sub-heading) *Acetic acid alcohol mixture*	*Oxalic acid etc.*
201	Table III, column 9 (under sodium hydroxide)	of coagulum	of coagulation
202	Table IV under Alum (a)	(a) with 0.01% soln.	(a) with 0·05% soln.
239	Table IV	const. conc. of Na tartrate=0.42N	const. conc. of Na tartrate=0.042N
	,,	conc. of I_2	conc. of Na tartrate
	Table V, column 3	$k'30$	$k'60$
240	26	Effect	Effects
243	5	cations and from	cations from
244	Fig. 6, ordinate	0.55	0.53
348	2	(Part V)	(Part IV)
	14	*Insert* "or solution" *before* gum acacia	
349	22	acacia	accia
	7	long range of concentration (6.5×10^{-3}g to 3.9×10^{-6}g) was verified by	"long range .... drawn by
350	Fig. 2	conc $\times10^{-5}$g.	conc. $\times10^{5}$g.
351	13	dried at 105°	dried at 100°

RECENT RESEARCHES IN THE FIELD OF HORMONES AND THEIR APPLICATION TO THE MANUFACTURE OF GLANDULAR PRODUCTS IN INDIA*

BY PROF. B. B. DEY, D. Sc., F. I. C., F. N. I.

Nowhere in the whole domain of pure chemical science has intensive research, carried out during the past few decades, led to more fruitful and astonishing results than in the field of hormones. Abel[1] gave us crystalline adrenaline from the adrenal glands of oxen in 1901, and Kendall[2] isolated crystalline thyroxine from the thyroid glands of cattle in 1914. In 1921 Banting and Best[3] isolated from the pancreatic glands of dogs and foetal calves potent extracts of insulin which in combination with zinc can now be had in the form of pure crystals. Since 1920 rapid strides have been made in our knowledge of the chemistry of the pituitary gland[4]; oxytocin and vasopressin have been successfully fractionated and are now available in concentrated and almost pure forms and some of the anterior pituitary hormones are also claimed to have been isolated in the crystalline form. The years 1930 to 1943[5] witnessed the isolation of an array of crystalline steroid hormones—the androgens, the œstrogens, the progestational hormones and the cortical hormones. Liver extracts[6] are now available in extremely concentrated forms, one c.c. of which administered parenterally keeps the anaemic patient fit for weeks together. These great achievements have been made possible only by the successful and harmonious co-operation between the chemists on the one hand and the clinicians on the other.

I propose in the course of this lecture to dwell briefly on the salient features of the developments in this field, considering them as far as possible in the sequence in which they have been taking place.

ADRENAL GLANDS

Taking first the adrenal gland hormones for consideration, we find that there are two of these glands situated like pear-shaped caps above the two kidneys.

The whole gland consists of two parts, the medulla and the cortex, the adrenaline being concentrated entirely in the medulla. The morphological characters of these glands obtained from some of the South Indian animals are shown in Fig. 1.

It will be noted that while the adrenal glands of sheep are of a uniform oblong structure, those of the cattle are uneven in contour showing deep clefts in many cases. Again the left adrenal differs in appearance from the right and the adrenals of the ox often show a marked difference in shape from those of the buffaloe. The following table (Table I) gives the average weight of the adrenal glands, the percentage content of the medullary tissue and the adrenaline content (mg. per gram of whole tissue) of the animals from the Madras slaughter house.

* Presidential address delivered at the 20th Annual General Meeting of the Indian Chemical Society held on January 4, 1944 at Delhi.

TABLE I

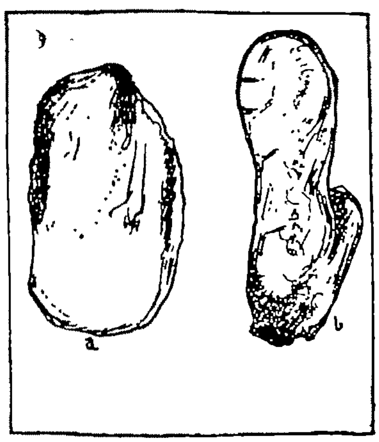
Adrenaline contents of glands.

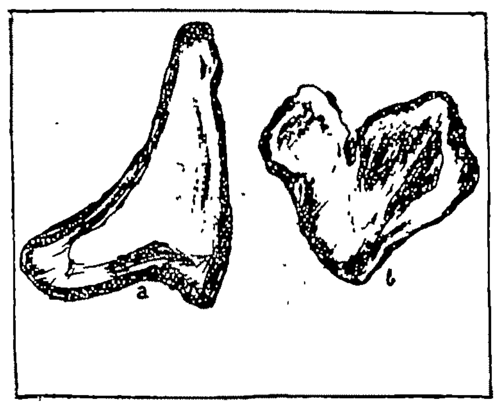
	Average wt. of gland in g.	Percentage of medullary tissue.	Adrenaline content (mg/g.)
Cattle	8—10	25—29	1·85
Sheep	1·5—2·5	17—20	1·57
Pig	2—4	17—20	0·8

That extracts of adrenal glands possessed the property of raising the blood pressure was the first startling discovery made as early as 1894 by Oliver and Schafer[7] which aroused the great interest of chemists and stimulated research in gland products in general. Fundamental work on the preparation of the active principle was carried out in Abel's laboratory in Baltimore although the actual isolation was achieved in the research laboratories of Park Davis & Co. in 1901 by Aldrich[8] who had previously been an assistant in Abel's laboratory and by Takamine independently of each other. The elucidation of its constitution by analytical means was soon followed by synthesis, Dakin's process[9] starting from catechol being now actually employed by several commercial firms.

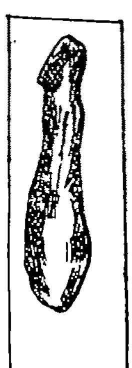
Fig 1
Adrenal gland.

Adrenal gland (left side)
(a) Buffaloe ; (b) Cow

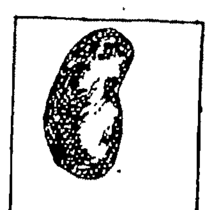




Adrenal gland (right side)
(a) Buffaloe ; (b) Cow.



Pig.



Sheep.

The natural process of preparation from glands is commonly based on the solubility of the base in acidified solvents like alcohol, the free base being thrown down from these

extracts by the cautious addition of ammonia. Being crystalline, the substance can be readily purified and the purity checked by melting point and optical rotation, and also by colorimetric assays and ultimately confirmed, when necessary, by bio-assay.

Our annual requirements of adrenaline in normal times have been estimated to be of the order of 10 kgs. of the free base. From Table V it will be evident that in normal times of peace the slaughter houses of ten of our major cities, Bombay, Calcutta, Delhi, Madras, Hyderabad, Lahore, Karachi, Lucknow, Dacca and Bangalore, handle annually about 320,100 cattle which will yield about 3,201,000 g. of adrenal tissue and about 3,071,500 sheep which in its turn will yield about 6,143,000 g. of adrenal tissue. From this total of approximately ten thousand kilograms of adrenal tissue, a net amount of over 10 kg. of pure adrenaline can easily be isolated. It seems, therefore, that India ought to be self-sufficient as regards at least her own needs of this most valuable drug.

Although closely related compounds possessing the sympathomimetic action of adrenaline have been prepared either synthetically or from natural sources, the most important of these being ephedrine, none of them have been able to replace adrenaline which is one of the essential and most powerful drugs of the present day.

THE CORTEX

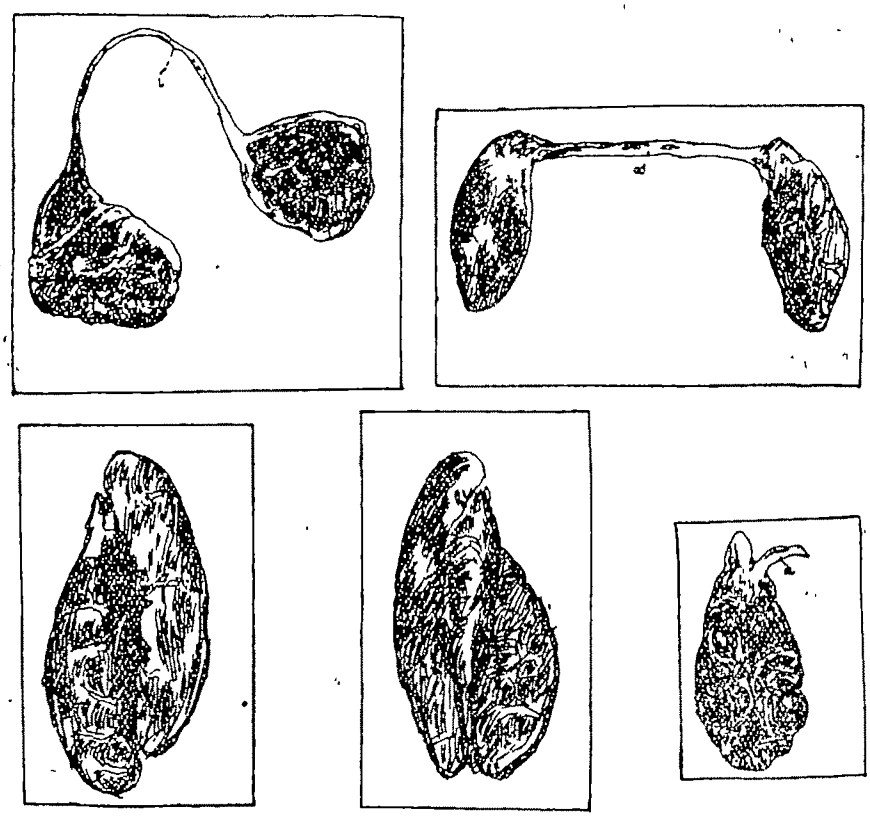
The adrenal cortex, unlike the medulla, is considered to be essential for life as it controls the vital metabolisms of carbohydrate, salt and water. No single substance which can be described as the vital hormone of the cortex is elaborated by the gland but a surprisingly large number of closely related compounds having specified effects, qualitatively different one from the other, have been prepared from it. The intensive researches carried out during the last seven years (1935—1942) by three different groups of workers—Kendall (America), Wintersteiner (America) and Reichstein (Switzerland[5]) have resulted in the isolation of a series of crystalline compounds from the adrenal cortex, typical examples of which are corticosterone, dehydrocorticosterone and desoxycorticosterone. Their constitutions have been established beyond doubt and one of these, desoxycorticosterone, is now synthesised and made available for clinical use. For medical purposes, however, a whole extract of the cortex containing all the hormones in a fairly pure and concentrated form and known popularly as Cortin is preferred.

Statistics are not available regarding the requirements of cortical extracts in India, but there is no doubt that enough extract can be manufactured for supplying all our needs. The methods of extraction are rather complicated, involving as they do initial extraction with lipoidal solvents, scrupulous removal of the last traces of adrenaline and final purification by fractional distribution between different organic solvents.

THE THYROID GLAND

The thyroid gland consists of two lobes, situated on either side of the wind-pipe connected usually by a narrow isthmus. The morphological characters of those of some of the South Indian animals are shown in Fig. 2.

Fig. 2
Thyroid gland.



Cattle thyroid (1=isthmus)

Sheep. (a = isthmus)

Pig. Pig. Sheep. (a=isthmus)

It will be noted that the thyroid glands in the case of both cattle and sheep possess a long and narrow isthmus, whereas in the case of the pig, the two lobes are fused together lengthwise. The description given in literature that the shape of the thyroid glands resembles that of a purse with the flaps opened up seems to apply, therefore, only to the pig thyroids.

Thyroid is most commonly and probably, best, administered as the desiccated whole gland. The fresh glands are cleaned free from fat and connective tissues, dried at a temperature not exceeding 60°, defatted with a solvent like petroleum ether and diluted with lactose so that the final product has a thyroxine-iodine content of 0·1%. Thyroxine itself is, however, indicated in acute cases of thyroid deficiency and also in those few cases where oral doses of the desiccated gland are not tolerated. The isolation of thyroxine is by no means easy, involving as it does hydrolysis with graded strengths of baryta and final purification through the sodium salt. Thyroxine itself is insoluble and is, therefore, always administered parenterally as the sodium salt.

It was discovered in the course of these investigations that thyroid glands of local animals contained a higher proportion of total iodine and thyroxine-iodine than those reported of animals in Europe, and this observation has been independently confirmed from the Biochemical Standardisation Laboratory, Calcutta[18].

The following table (Table II) represents the total iodine and thyroxine-iodine contents as well as the absolute weights of the glands of cattle, sheep and pigs, obtained from the Madras slaughter house.

TABLE II

Iodine content of desiccated thyroid gland.

	Average weight of glands.	Total iodine.	Thyroxine iodine.
Cattle	9—10g.	0·91%	0·35%
Sheep	1·5—2	0·66	0·26
Pig	3—6	0·84	0·39

These values may be compared with the figure 0·235% for the thyroxine-iodine of a standard specimen of desiccated thyroid obtained from the British Drug House in London.

The efficacy of the whole gland for the correction of myxoedema was established as early as 1891 by Murray, but the supposed active principle, thyroxine, was isolated by Kendall[9] in pure crystalline condition only at the end of 1914. Nearly a decade later Harington[11] interested himself in the subject and soon worked out a method for the isolation of the hormone in very much better yields. He also established its correct structure and in collaboration with Barger, ultimately succeeded in synthesising the hormone—a synthesis which is now being adopted by some of the commercial firms in Europe. The satisfaction of the chemist in having isolated the real hormone of the gland was, however, rather short-lived, as it was soon found that the whole thyroid gland was more active than 'pure thyroxine' on an equi-iodine content basis. The consensus of opinion at the present day is that the real hormone of the thyroid gland is either thyreoglobulin itself or an intrinsic part, thereof, most probably a complex peptide made up of the following components in its structure. (Thyroxine radical—Amino acid radicals—Diiodotyrosin radical).

The assay of thyroid extracts is best carried out chemically by estimating the total organic iodine, the modern view being that the physiological potency of thyroid is dependent more on the total organic iodine than on the thyroxine-iodine. The chemical assay can always be checked, if necessary, by one of the several biological methods, the most accurate being that based on basal metabolism.

Fortunately enough, thyroid deficiency diseases are rare in India and enough thyroid is available, say from the Madras slaughter houses alone, to treat perhaps all the cases of thyroid deficiency occurring throughout India.

Attempts have been made to iodinate proteins in order to obtain synthetic iodo compounds, which would simulate the natural thyreoglobulin in physiological activity. Success was finally achieved in 1939 by two German chemists, Ludwig and Mutzenbecher[14], who iodinated casein under carefully controlled conditions and obtained a product which showed thyroid activity. This product and the concentrates obtained by its hydrolysis have been prepared in this laboratory and are being put to trial in some of the clinics in Madras. Ludwig and Mutzenbecher succeeded in isolating crystalline thyroxine itself by hydrolysis of this portein—a remarkable discovery which has been confirmed now by

Harington[15]. The synthesis of thyroxine *in vivo* from the diiodotyrosine molecule has also been experimentally established very recently[16].

The fate of iodine in the body, its absorption by the thyroid gland and the subsequent changes are now being investigated in American laboratories by a novel technique, namely, by the use of radioactive (labelled) iodine[17]. These researches hold out promise of important developments not only in the field of pure chemistry, but also in its clinical applications.

THE PARATHYROID GLANDS

The parathyroid glands, which are the smallest of the ductless glands, consist of two pairs of glands, one pair lying on each side of the neck, close to the thyroid or embedded in it.

No pure chemical individual has yet been isolated from the parathyroid. "Parahormone", which contains the active principle (of a protein type) in a rather crude form, is usually obtained by Collip's method[9], where the fresh glands are minced and extracted with dilute hydrochloric acid at 100°, the mixture is cooled and the solidified fat, etc, removed by filtration. Inert protein is now removed by precipitation by adjusting the p_H to 5·5.

The filtrate containing the active principles is adjusted to Congo-red p_H and saturated with NaCl, when parathormone is obtained in a solid form. This is dissolved in very dilute hydrochloric acid and sterilised by passing through Berkfeld filter and administered by the intravenous or the subcutaneous route. The active principle is isolated sometimes also as the picrate, as in the case of insulin.

The parathyroids are concerned with the regulation of the calcium metabolism and the controlling of the concentration of calcium and phosphorus in the blood serum. Deficiency of the secretion leads to acute symptoms of tetany, which is characterised by a decrease in the serum calcium.

Cases of parathyroid deficiency do not appear to be very common in India, and it is certain that enough extracts for our needs can certainly be prepared by mobilising the glands of some of our slaughteries.

Substitution therapy with parathyroid extracts has now been largely replaced by treatment with irradiated sterol derivatives, the most important of which is dihydrotachysterol known popularly as A. T. 10.

THE PANCREAS

The importance of the discovery of insulin and its application as a drug can hardly be overestimated. The history of the investigations of Banting and Best on the hormones of the pancreas in Professor MacLeod's laboratory in the University of Toronto, the preparation of potent extracts having powerful hypoglycemic action from the pancreas of foetal calves in 1921, and the taking out of patents for the manufacture of insulin by the Insulin Committee appointed by the Toronto University in 1923 are now generally all known

Insulin is now prepared from fresh pancreas by processes involving preliminary extraction with acidified solvents, removal of protein impurities by precipitation with graded strengths of alcohol, followed by isoelectric precipitation or purification through the picrate. The final product after bio-assay is sterilised by filtration.

The maximum concentration of insulin is found in foetal calves and diminishes progressively with the age of the cattle. This is illustrated in the following table (Table III) containing yields of insulin in international units per g. of tissue from the pancreas of cattle of different ages.

TABLE III

Foetal calves up to 5 months	...	...	33 I. U.
Foetal calves between 5 and 7 months	...	...	23
Calves from 6 to 8 weeks	...	..	11·5
Cows 2 years old	...	...	5
Fully grown animals	...	...	2

Certain classes of fish known as the Teleostoi, the cod being a typical example, in which the islet tissue exists separate from the main pancreatic gland, yield 15 to 30 units of insulin per gram of tissue which is nearly 10 times the yield obtained from the pancreas of domestic animals. The suggestion that the islets of fish might furnish a convenient practical source of insulin was first made by MacLeod and this aspect of the subject was investigated by McCormick and Noble in America and by Dudley in England in connexion with the fisheries of these two countries[19].

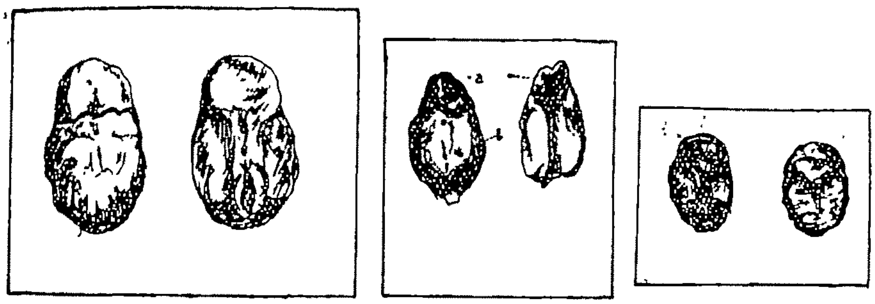
It is doubtful if locally made insulin has ever been put on the Indian market. Researches on its preparation are being pursued in the laboratories of the Indian Institute of Science, and there is every reason to hope that these researches will lead to the production of insulin on a sufficiently large scale for our requirements. The possibility of utilising the raw material of our fisheries for the production of insulin and also of protamine also needs careful investigation.

Attempts made to prolong the action of insulin in subcutaneous doses so as to avoid giving frequent injections led to the introduction of Protamine-Insulin by Hagedorn[20] in 1935 and its modification by Scott[21] into Protamine-Zinc-Insulin in the following year. These together constitute perhaps the greatest advance in the treatment of diabetes mellitus since the discovery of insulin itself. Hagedorn and his co-workers in Copenhagen carried out a series of experiments on the solubility of insulin combined with different protamines and succeeded in producing a protamine-insulin suspension which when injected subcutaneously is absorbed considerably more slowly than soluble insulin hydrochloride and thus exerts a more prolonged hypoglycoemic action. This substance termed protamine-insulin was improved upon still further by Scott and Fisher who on the results of experiments on the zinc contents of insulin preparations tried the effect of adding small quantities of zinc salts to protamine-insulin. As a result of these researches, the new compound Zinc-Protamine-Insulin has been introduced into practice. The standard consists of a batch of zinc-insulin crystals, one milligram of which contains by international agreement 22 units of insulin.

THE PITUITARY GLAND

The pituitary gland, situated in a cavity "Sella turcica" at the base of the brain, produces a battery of hormones and has been described, perhaps aptly, as the leader of the endocrine orchestra. The following photographs (Fig. 3) illustrate the morphological characters of the pituitary glands of cattle, sheep and pigs obtained from the Madras slaughter house.

Fig. 3
Pituitary gland



Cattle. Sheep. Pig.
[a = Posterior lobe ; b = Ant. lobe]

The pituitary is made up of two parts termed the anterior and the posterior lobes which elaborate entirely different principles. The following table (Table IV) gives the average weight of the pituitary gland, and the ratio of the anterior to the posterior lobe, in the case of the glands of animals obtained from the local slaughter house[10].

TABLE IV

	Average weight.	$\frac{\text{Anterior lobe}}{\text{posterior lobe}}$
Cattle	0·8—1·5 g.	2·3—2·8
Sheep	0·3—0·4 g.	8—11
Pig	0·2 g.	1·2—1·5

It will be apparent from the table that sheep are comparatively poor sources for the posterior lobe. They are, however, ideal for the isolation and studies of the anterior lobe principles. Figures available in literature go to show that ox-pituitaries of European animals weigh on the average 2·5 grams, the posterior lobe weighing only 0·5 g. It will thus be seen that while the pituitary glands of local cattle weigh less, the ratio of the posterior to anterior lobe is definitely higher.

Pituitrin, one of the indispensable drugs of the present day, is isolated from the posterior lobe. The method is simple, involving the extraction of the dissected posterior lobes or the desiccated posterior powder with 0·25%. acetic acid the concentration being so adjusted that each c.c. of the fluid extract contains 10 international units. In 1928 Kamm[22] fractionated pituitrin into (*a*) oxytocin which stimulates the uterus, and (*b*) vasopressin which raises the blood pressure, but more recent investigations tend to show that the posterior pituitary elaborates one single hormone which gets split up into various fractions during the processing. In 1942 Van Dyke and his colleagues[23] isolated a protein from the

posterior lobes of frozen ox pituitaries which they claim is pure and which contains all the active fractions.

The annual requirements in India of posterior pituitary extracts correspond at present to about 2,500 grams of the dried posterior powder. This amount can certainly be produced by tapping the resources of only a few of our larger slaughter houses

Dried posterior pituitary powder, prepared in this laboratory, has been found on bio-assay to correspond with the international standard.

THE ANTERIOR PITUITARY LOBES

The anterior pituitary can be processed to give a number of hormones, all of which are supposed to be of protein nature and some of which are claimed to have been prepared in the crystalline condition[24]. The more important of these are the lactogenic, the gonadotropic and the thyreotropic principles. The least encouraging situation to-day is the clinical application of the experimental findings in the field of anterior pituitary hormones. Although those findings have certainly improved our diagnosis of pituitary disorders in man, they have added little to their control. It may at least be said that we have not scored a success in pituitary therapy comparable to that of the thyroid, pancreas and adrenal glands.

THE SEX HORMONES

The production of definite endocrine secretions by the sex glands had been guessed for a long time, spayed and castrated animals showing atrophy of the sex characteristics if they were mature, or failing to develop the secondary sexual characteristics if they were immature. The actual isolation of the various hormones was, however, delayed for a long time, principally on account of the extremely low concentration in which these principles were found in the actual glands. Between the years 1925 and 1930 a number of happy discoveries was made such as that of pregnancy urine as an exceptionally rich source of the œstrogenic hormones, the elaboration of the vaginal smear test for the œstrogens and the capon comb test for the androgens, etc., which made possible the successful isolation in crystalline form of the various œstrogenic, androgenic and progestational hormones[25]. Typical examples of these are œstrone, œstradiol, testosterone and progesterone. For clinical use œstradiol is obtained from pregnancy urine. Œstrone is manufactured from the urine of pregnant mares, testosterone from testicular tissue and also synthetically from cholesterol and progesterone only synthetically from stigmasterol, since the supply of *Oorpora lutea* is strictly limited.

Even after the pure hormones were isolated, the clinician was confronted with many new problems. The hormones were rapidly absorbed by the blood stream and were often excreted as such in the urine or detoxicated by the liver, even when administered parenterally. In the hope of finding some product whose action would be slow, steady and prolonged and thus simulate the function of the natural healthy glands, various esters of the hormones were prepared some of which have been successful and now introduced into practice. Œstradiol is now administered as the benzoate and testosterone as the propionate or the methyl ester. The latest innovation in the field of sex hormone therapy consists in the actual implantation of tablets by making incisions in the skin of the

hypogastric region and embedding sterilised tablets of the hormones inside and suturing up the skin with cat-gut ; these pellets have been claimed to be active for months.

. Although the sex hormones are now finding use in the treatment of various sex disorders both in man and in woman, and also for the correcttion of hypogonadism[26], their use in clinical practice may be considered to be still in the experimental stage. Several synthetic substances like hexestrol and stilbestrol have also come into the market, and some of these are claimed to be effective even on oral administration. The greatest caution has, however, to be exercised in the use of these synthetic substitutes as reports of untoward symptoms or of their acting even as cumulative poisons are not uncommon.

LIVER AND STOMACH EXTRACTS

The efficacy of liver for the cure of pernicious anaemia was discovered by Minot and Murphy[27] in 1926. About eighteen years have lapsed since that time and we are still in the dark as regards the chemical nature of the active principle or principles. For working in this field the chemist has to face very heavy odds since the only satisfactory method of assay is the clinical test on pernicious anaemic patients, animal experiments having proved far from satisfactory. It can be claimed, however, that liver extracts are now available in highly purified forms, the amount of material needed by the patient per day being decreased from 400 g. to less than 10 mg.

Dr. Cohn[28] of the Harvard Medical School was the first to isolate in 1927 an active fraction (Fraction G) from whole liver by methods involving the removal of the gross impurities by heat coagulation and treatment with alcohol. An amorphous powder was obtained which had the properties of nitrogenous base. Dakin and associates [29, 30] took the concentration a step further by using Reinecke salt to effect the precipitation of the active fraction. Hydrolysis of the product yielded a series of amino-acids and Dakin came to the conclusion that the haemopoietic principle of the liver is, or is associated with, a peptide possessing many of the properties of an albumose.

During the years 1936-42 several groups of workers[31] have been working on the subject, namely, Subbarow and Jacobson in Boston, Laland and Klem in Strendell's laboratory in Oslo, and Paul Karrer in Zurich. The active principle was quantitatively adsorbed by charcoal and eluted by means of phenol. These researches go to show that the active principle is of a multiple nature ; continued fractionation of liver extracts resulting in partial or complete extinction of therapeutic activity which was recovered by admixture of the purified materials with the other fractions. These fractions have been termed accessory factors, for while like co-enzymes they are by themselves therapeutically inert, they augment the activity of the primary factor or factors contained in the purified fractions. Up to now four such accessory factors, isolated from crude liver preparations, have been identified, *viz*, (1) *l*-tyrosine in a yield of 6 mg., (2) a complex purine of the pterine class, (3) a peptide in a yield of 14 mg. and (4) tryptophane in yields of 5 mg. each per 100 g. of whole liver. The primary factor itself is considered to be a complex pyridine compound.

The fact that pernicious anæmia is associated with diseases of the stomach has been known for some time. In 1929 Castle[32] showed that meat which had been digested with stomach would cure pernicious anæmia although raw meat would not. He postulated the

presence in gastric juice of an enzyme 'Haemopoietin' or the "intrinsic" factor which reacted with an "extrinsic" factor in the meat with the formation of the P. A. factor, which is then absorbed and stored in the liver, probably after suitable modification. Recent researches have largely confirmed Castle's hypothesis ; there is an antianaemic "liver principle" and an antianaemic "stomach principle" and both are capable of relieving pernicious anaemia. These two antianaemic principles, *Anahaemin* and *Haemopoietin* as they have been called, although quite distinct are closely related in certain respects. The liver principle is a thermostable substance, relatively stable to many reagents and solvents and moderately resistant to digestion with trypsin, pepsin and erepsin. Haemopoietin, on the other hand, is a thermolabile enzyme, distinct from pepsin and rennin and always associated with protein; it is relatively unstable and very easily destroyed by chemical reagents and many solvents and by enzymes such as pepsin and trypsin and by heating to 60°.

Pernicious anaemia is due primarily to the deficiency of the intrinsic factor and so the treatment consists in either supplying the intrinsic factor in the form of stomach preparations whereby the elaboration of the haemopoietic principle by the stomach is stimulated or by the actual administration of the pre-formed active principle in the form of liver extracts.

Liver and stomach extracts are widely used in India for the treatment of anaemia and a variety of other diseases. Liver extracts which are available for either parenteral or oral use, are processed by extraction of fresh liver with alcoholic solutions, followed by precipitation and removal of the protein impurities. The preparation of stomach extracts involves the desiccation of the lining of the stomach at a sufficiently low temperature. Potent extracts of liver and stomach have now been placed on the market by several commercial firms in India, but very few of them are believed to be as successful as the German and American preparations.

From the brief review given in the preceding pages, it will be clear that gland products like adrenaline, insulin, pituitrin, liver extracts, etc., have become indispensable for the welfare of any community in the modern age, and added importance has to be attached at the present moment to some of these drugs, as they have become of urgent importance in connexion with the war. It was, therefore, in the fitness of things, that a comprehensive scheme of research into the preparation of gland products in India was subsidized by the Board of Scientific and Industrial Research early in 1941.

THE CATTLE WEALTH OF INDIA

The cattle population of India is considered to be one of the largest ; India being supposed to possess almost a third of the world's cattle. The raw material for the production of gland products may, therefore, be drawn in large quantities from our slaughter houses where the domesticated animals are killed daily for human consumption. The following table (Table V) represents the average peace-time statistics of the animals slaughtered every year in some of the more important cities in India.

TABLE V

Number of animals slaughtered per year.

	Buffaloes, bullocks, cows and calves.	Sheep and goats		Buffaloes, bullocks, cows and calves.	Sheep and goats.
Bombay	84,800	799,000	Lahore	17,900	247,000
Calcutta	83,000	230,000	Karachi	16,400	195,000
Delhi	54,000	384,000	Lcuknow	10,000	149,000
Madras	1,9000	468,000	Dacca	16,500	47,600
Hyderabad	18,200	498,300	Bangalore	--	53,600

These are only approximate figures and the numbers must now have considerably increased due to the present military situation and the necessity for exporting dehydrated meat to foreign countries. The table reveals the important fact that a large and steady supply of raw material is available in India even in normal times of peace for the large scale production of glandular products and that a central factory for their manufacture might profitably be started in one of the major cities like Bombay, Calcutta, Delhi or Madras.

THE ORGANIZATION OF THE SLAUGHTER HOUSES.

The organizations which have been perfected in the abattoirs of Europe and in the packing houses of America, are, however, completely absent in the slaughteries in India. Although several thousands of animals are killed daily in our cities, there are hardly any facilities existing at present for the collection and preservation of the glands, so that they might be worked up later or sent to a distant place where the factory for the production of glandular products would be situated. Insulated chambers, cooled by refrigerating machinery, are the essential features of all modern abattoirs. Immediately after the animals are killed, the dressed carcasses are removed to the cold room, where they are kept for several hours during which time all the endocrine glands are skilfully removed under expert supervision. These are, then, frozen and conveyed in iced and insulated trucks to local firms, if there are any, or packed into large refrigerated chambers in ships, which take them to distant countries across the seas. In our country, on the other hand, there are hardly any slaughteries which can boast of insulated cold rooms with the result that there is little time available for the selection and removal of the glands which in several cases have their potent principles destroyed to a large extent even by one hour's delay of removal, on account of the setting in of autolysis.

To give one illustration, we may consider the case of the pituitary gland. To dissect this out, the skull has to be opened and the brain exposed, a process during which the matter of the brain undergoes rapid deterioration at the ordinary temperature, and is thereby rendered unfit for human consumption afterwards. If, on the other hand, our slaughteries had been furnished with suitable refrigeratory systems, these brains, after the removal of the pituitary, could easily have been kept frozen without the slightest change or loss of freshness until demanded by the public. From the fact that in some of the coastal parts of India, fish is being successfully refrigerated and supplied in a fresh condition to the interior parts, it will be evident that the introduction of refrigerated chambers in our slaughter houses should permit a similar transport not only of glands for commercial purposes, but also of meat for domestic consumption, in perfect condition of freshness and flavour from the larger cities to the interior parts.

PRESERVATION AND STORAGE OF GLANDS

The major slaughteries in India are widely scattered and for the processing of glands in a central factory, we have to study the best conditions for the storage The tropical heat prevailing in our country militates against the possibility of keeping the dissected glands for any length of time at the ordinary temperatures. Again, the different glands vary as regards the stability and susceptibility to change of the particular hormones concerned. In the case of these glands whose hormones are specially sensitive, e. g. in the case of insulin, the extraction must be commenced immediately. In the case of certain other glands like the adrenal and the parathyroids, the glands can be frozen immediately after dissection and transported in this condition to the laboratory or factory.

Investigations carried out in these laboratories[33] have shown that frozen adrenal glands preserve for several days and that even after a fortnight's storage in the frozen condition, the loss in adrenaline content is not serious. The actual data are given in the following table (Table VI)

TABLE VI

Changes in adrenaline content when the glands are kept frozen.

Period of storage.	Adrenaline content (mg/g. of gland persulphate colour reaction).
Fresh glands	1·85
Frozen glands stored for one day ...	1·72
Frozen glands stored for 1 week ...	1·58
Frozen glands stored for 2 weeks ...	1·51

Similarly freezing appears also to preserve the potency of pituitary glands[34]. In the following table (Table VII) are given values for the vitamin-C contents of the pituitary glands which have been stored for varying periods in the frozen state. The loss in the vitamin content is not very appreciable even after two weeks' storage and it is possible that physiological potency, too, is affected only to a similarly slight extent.

TABLE VII

Change in vitamin-C content in frozen pituitary glands.

Period of storage	Vitamin-C content (mg/g. of fresh gland).
Fresh glands	1·30
Glands kept frozen for 1 day	1·28
Glands kept frozen for 1 week	1·16
Glands kept frozen for 2 weeks	1·16

In the case of the posterior pituitary, the active principles are not soluble in organic solvents, so that the tissue can be conveniently dried by treatment with successive batches of acetone and in the final dried condition the powder can be stored for several months, especially when kept at a low temperature and out of contact with air.

In the case of the thyroid gland, the active principle is stable towards heat and is insoluble in lipoidal solvents, so that the glands can be successfully desiccated, *i. e.*, dried at fairly high temperature and then defatted and preserved until ready for subsequent processing.

It has been definitely proved from our experiments[34] that the active principles of the thyroid gland possess a remarkable stability. Figures which are reproduced in the following table (Table VIII) show that the value for thyroxine-iodine and for organic-iodine percentages are fairly constant irrespective of whether the glands have been chilled in dry ice immediately after the animals were slaughtered, or stored frozen for one month, or even whether the desiccated glands have been stored at the ordinary temperature (30°) for two years.

TABLE VIII

Condition.	Thyroxine-iodine (% total iodine).	Organic-iodine (% total iodine).
Cattle glands brought to the laboratory chilled in dry ice and desiccated immediately ...	39·86	98·33
Cattle glands frozen for one month ...	40·14	97·93
Desiccated cattle glands stored at 30° for 2 years	39·86	98·20

THE MAKING OF A DRUG.

The glandular principles have, in several instances, to be administered parenterally, and moreover, as they are potent in minute doses—sometimes even in fractions of a m g.—the greatest care has to be exercised in the control of dosage of the drugs. In the case of adrenaline and thyroxine, the products can be obtained in a pure crystalline condition and the final solutions can be made with accurately weighed quantities of the solids. Not so, however, is the case of certain other principles like insulin, liver extracts and pituitrin, for the assay of which suitable chemical, physical or physicochemical methods are not available. In these cases the finished products have to be biologically assayed and then properly dosed. Even when chemical methods are available for the assay of a hormone (e. g the colorimetric method for the estimation of adrenaline), the final check must always be made with a biological method. A biological standardization department is, therefore, an essential pre-requisite of an up-to-date factory for the manufacture of glandular products. The importance of biological standardization of drugs has been critically reviewed by Dr. B. Mukerji[35] of the Biological Standardization Laboratory, Calcutta, in a recent editorial article in the columns of 'Current Science'.

SUMMARY AND CONCLUSIONS

No serious attempt has yet been made to tap the vast wealth of the slaughter houses in India. The raw material available in these places, if properly utilized, should not only supply all our requirements of such essential drugs as adrenaline, pituitrin, etc., but would also yield a variety of useful articles, such as meat extracts, gelatin, pepsin, trypsin, rennet, etc., not to mention the commoner products such as glue, manure, etc.

On account of the stress of the present abnormal circumstances due to the war, isolated efforts are no doubt being made by several laboratories and firms in India to

manufacture some of these gland products. It is doubtful, however, if the industry would be able to survive the serious post-war competition of the drug houses of Europe and America which is inevitable, unless our slaughteries are thoroughly overhauled and organized in the meantime with such safeguards of state control as may be essential and an exhaustive study of problems of storage and transport of the glands in Indian climatic conditions made, so that it becomes practicable to establish either a large central factory in India or several provincial factories, e.g. in Calcutta, Bombay, Madras and Delhi, where the glands from the numerous slaughteries could be collectively or individually processed.

A word may be added in conclusion regarding the suitability of manufacturing hormones synthetically in India. Considering the fact that our heavy chemical industry is still in its infancy and that there has been hardly any development yet in the manufacture of fine chemicals worth mentioning, it seems obvious that it would not be possible for many years to come to synthesise such complex drugs as hormones without importing many of the intermediate fine chemicals required for the purpose. We are, on the other hand, more favourably situated than most other countries in respect of our unbounded natural resources awaiting utilization, and the prospects, therefore, of starting the industry in this country from animal glands would appear to be definitely brighter.

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ADDENDA

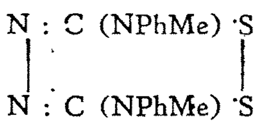
Page.	Para.	Line.	*for*	*Read*
1	2	3	"...taking place"	"...taking place, and on their possibilities in India."
3	4	1	"extracts"	"hormones"
3	,,	2	*omit* "extracts"	
3	4	3	"extraction"	"isolation"
3	5	1	"situated"	"situated at the neck"
4	1	4	...	*Read* "approximately" *after* "therefore"
5	3	13,14	...	"Structure : Thyroxine : Amino-acid radicals : Di-iodotyrosin"
6	1	3	"radio-active (labelled)"	"radio-active or labelled"
6	2	3	...	"actually embedded in it (see Fig. 2, sheep thyroid)".
6	6	2	*omit* "certainly"	
7	3	1	"Teleostoi"	"Teleostei"
8	1	2	...	*Read* "...has been aptly described as the leader......"
9		1		"...they claim to be pure and to contain all the..."
9	2	2	...	*insert* "in all respects" *after* "correspond"
9	4	9	"androgens, etc. which made"	"androgens etc. These made"
9	4	14	"synthetically"	"exclusively by syntheses"
10	1	3	*Insert after*	"stage" "The investigation of sex hormones requires careful organisation and is beset with considerable experiemental difficulties and so far as is known little progress has yet been made in India in this field"
10	3	4	*Insert* 'a' *before*	"nitrogenous"
11	[illegible]	1		*Read* the first line as "Anaemia is unfortunately

PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD —N·C·S—. PART XIII. ACTION OF SULPHUR MONOCHLORIDE ON *as*-METHYLPHENYLTHIOCARBAMIDE. FORMATION OF THIODIAZOLES

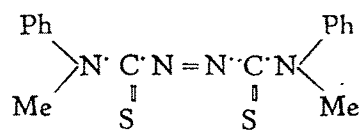
BY RAMCHANDRA SAHASRABUDHEY AND HANS KRALL

Sulphur monochloride reacts like bromine on arylthiocarbamides to give iminodihydrobenzthiazoles and not the compounds postulated by Dost.

By the action of sulphur monochloride on a chloroform solution of *as*-methylphenylthiocarbamide Dost (*Ber*., 1906, **39**, 1014) obtained the hydrochloride of a base with the composition $C_{16}H_{16}N_4S_2$, 2HCl for which he suggested the following constitutional formulae :



(I)



(II)

The hypothesis that disulphides are formed as unstable intermediate products in the oxidation of aromatic thiocarbamides to thiodiazoles has often been put forward (Patel and Chakravarty, *J. Ind. Inst. Sci*., 1930, **13**, 85 ; De and Chakravarty, *J. Indian Chem. Soc*., 1928, **5**, 661) and the work of Guha and others (Freund and Imgart, *Ber*., 1895, **28**, 946 ; Busch and Schmidt, *Ber*., 1913, **46**, 2240 ; Fromm and co-workers, *Annalen*, 1923, **434**, 285 ; 1923, **433**, 1 ; Guha, *J. Amer. Chem. Soc*., 1923, **45**, 1036) has shown that hydrazodithiodicarbonamides can be oxidised and cyclised to 1 : 3 : 4-thiodiazoles.

Dost's compound has been prepared with the object of studying its constitution, and also with the idea of converting it into a thiodiazole, if possible. It has now been found that it is identical with 1-imino-2-methyl-1:2-dihydrobenzthiazole (Besthorn, *Ber*., 1910, **43**, 1519 ; Hunter, *J. Chem. Soc*., 1926, 1392 ; *vide* experimental).

Phenylthiocarbamide gives in an analogous manner, 1-aminobenzthiazole (Fischer and Besthorn, *Annalen*, 1882, **212**, 326 ; Hugershoff, *Ber*., 1903, **36**, 3134 ; Hunter, *J. Chem Soc*., 1926, 1386).

The above results indicate that in a chloroform medium the action of sulphur monochloride on *as*-methylphenylthiocarbamide and on phenylthiocarbamide follows the same course as the action of bromine on these compounds in the same solvent studied by Hugershoff (*loc. cit.* *Ber* , 1903, 36, 3121 ; Besthorn, *loc. cit.*).

The action of sulphur monochloride on thiocarbamides and thioamides has also been studied by Chakravarty (*J. Chem. Soc*. 1923, 123, 964) in an absolute alcoholic medium and by Ishikawa (*Sci. Papers Inst. Phys. Chem. Res*., 1925, 3, 147) in cold ethereal solutions Further work is in progress.

EXPERIMENTAL

Action of Sulphur Monochloride on as-Methylphenylthiocarbamide.—Methylphenylthiocarbamide (3 g.) was dissolved in chloroform (12 c.c.), and sulphur monochloride (1·5 c.c.), dissolved in chloroform (5 c.c.) was gradually added. The mixture was thoroughly shaken and allowed to stand After about an hour crystals separated and the mixture was left overnight, losely corked. The hydrochloride of the base was filtered off and the free base precipitated by ammonia from an aqueous solution. It melts at 123° and gives a picrate, m. p. 229—30° as described by Dost.

Its identity with 1-imino-2-methyl-1 : 2-dihydrobenzthiazole was established by taking a mixed melting point with a sample prepared according to the method of Hunter (*loc. cit.*).

Action of Sulphur Monochloride on Phenylthiocarbamide.—Phenylthiocarbamide (3 g.) was suspended in chloroform (20 c.c.) and sulphur monochloride (1·5 c.c.) dissolved in chloroform (5 c.c.) was added to it. The mixture was vigorously stirred when a viscous turbid mass was obtained, which became clear after about an hour. It was left overnight losely corked when a crystalline substance separated. This was found to be the hydrochloride (m. p. 236-37°) of a base, m. p. 131°.

The identity of the base with 1-aminobenzthiazole was established by taking a mixed m. p. with a genuine sample when no depression was recorded. The acetyl and benzoyl derivatives were found to be identical with those of 1-aminobenzthiazole.

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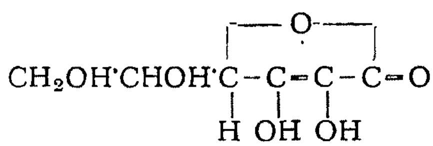
AUTO-OXIDATION OF ASCORBIC ACID IN PRESENCE OF VANADIC ACID, MOLYBDIC ACID AND TUNGSTIC ACID SOLS

By S. C. Shome

The auto-oxidation of ascorbic acid has been studied in presence of vanadic acid, molybdic acid and tungstic acid sols, in the *p*H range 3·5-4·3. It has been found that (*a*) vanadic acid sol in all concentrations accelerates the auto-oxidation of ascorbic acid and its activity is even greater than that of copper; (*b*) molybdic acid sol in low concentrations accelerates but in high concentrations inhibits the auto-oxidation of ascorbic acid; (*c*) tungstic acid in all concentrations inhibits the auto-oxidation of ascorbic acid.

During the last few years a large amount of work has been done on the physiological action as well as on the various physicochemical properties of ascorbic acid. Herbert and co-workers (*J. Chem. Soc.*, 1933, 1270) made for the first time a careful investigation of some of the physicochemical properties of ascorbic acid obtained from nature. Ghosh and Rakshit (*Biochem. Z.*, 1936, **289**, 15; 1937, **294**, 395; 1938, **297**, 153) have made a detailed and thorough investigation on the auto-oxidation of ascorbic acid.

The constitution of ascorbic acid as given in (I) is now generally accepted as correct.



(I)

The hydroxy groups attached to the double-linked carbon atoms have the remarkable property that they are capable of easy oxidation and stepwise dissociation into H^+ ions. Kellie and Zilva (*Biochem. J.*, 1935, **29**, 1028), Barron and co-workers (*J. Biol. Chem.*, 1936, **112**, 625) found that recrystallised natural ascorbic acid, free from the last traces of copper and iron, did not undergo any auto-oxidation up to *p*H 7·6. Ghosh and Rakshit (*loc. cit.*), however, found that carefully purified synthetic ascorbic acid, when dissolved in purest water, oxidised in air at *p*H above 3 and at *p*H range 5·8 to 7·2, 70-90% auto-oxidation took place in an hour. Sulphydrill compounds, chlorophyll, amino-acids and alkali cyanides inhibit the auto-oxidation of ascorbic acid, while copper and iron were found to be strong catalysts in the auto-oxidation of ascorbic acid. Dekker and Dickinson (*J. Amer. Chem. Soc.*, 1940, **62**, 2165), have studied the oxidation of ascorbic acid by oxygen with cupric ion as catalyst and explained the mechanism of the catalytic activity of copper. Lyman, Schultze and King (*J. Biol. Chem.*, 1937, **118**, 757) found that the catalytic oxidation of ascorbic acid by copper in presence of meta-phosphoric acid was inhibited. Mawson (*Biochem. J.*, 1935, **29**, 569) studied the auto-oxidation of ascorbic acid in presence of extracts of tissues and found strong inhibition. Giri and Shourie (*Indian J. Med.*

Res., 1940, **27**, 685) found that protective mechanism existing in tissues, which protects ascorbic acid against catalytic oxidation by copper, was mainly confined to the colloidal constituents of the tissues.

The object of the present investigation is to study the influence of inorganic colloids like vanadic, molybdic and tungstic acid sols on the auto-oxidation of ascorbic acid.

EXPERIMENTAL

Preparation of Sols.

Vanadic acid sol was prepared by adding to a solution of sodium meta-vanadate. a little greater than half the molecular proportion of hydrochloric acid when a reddish yellow sol was produced.

$$4NaVO_3 + 2HCl \rightarrow Na_2O.2V_2O_5 + 2NaCl + H_2O$$

The concentration of the sol is expressed in terms of the concentration of V_2O_5.

Molybdic acid sol was prepared by adding to a solution of sodium molybdate about twice the molecular proportion of hydrochloric acid when a colourless sol was produced The concentration of the sol is expressed in terms of the concentration of MoO_3.

Tungstic acid sol was prepared by adding to a solution of sodium tungstate a little greater than one and a half molecular proportion of hydrochloric acid. The concentration of the sol is expressed in terms of the concentration of WO_3.

Ascorbic acid solution was prepared each day just before the experiments and its strength checked by iodine titration. The sols were prepared every day two hours before the actual mixtures were prepared.

When ascorbic acid was mixed with vanadic acid sol, the mixture first became green and then it turned to blue very quickly. When ascorbic acid was mixed with molybdic acid sol, a yellow colour was developed which with time became green and then blue. With tungstic acid sol ascorbic acid gave a yellow colour with orange tinge.

Since ascorbic acid is a strong reducing agent, the reactions between ascorbic acid and the sols were first studied. The reaction in each case was adjusted to pH 3·5 by the addition of dilute caustic soda solution. Pure ascorbic acid and the mixture of ascorbic acid and sol were placed separately in two similar flasks which were then filled with nitrogen. The flasks were then shaken in a shaking machine in the dark and the rate of reaction was followed by the decrease in the concentration of ascorbic acid with time. Ascorbic acid was estimated by pipetting out 1 c.c. of the reaction mixture in dilute hydrochloric acid and titrating with iodine solution using starch as indicator. It was found that ascorbic acid could be estimated in presence of reduced vanadic acid sol when dilute acetic acid solution was used instead of dilute hydrochloric acid solution.

P22768

TABLE I

Ascorbic acid = $1 \times 10^{-2} M$. Temp. = 24°. pH = 3·5.

Time.	Vol. of iodine solution ($1 \times 10^{-2} M$) = 1 c.c. of the reaction mixture.				
	Sol = nil	Vanadic acid ($3·5 \times 10^{-4} M$)	Molybdic acid ($1 \times 10^{-2} M$)	Molybdic acid ($1·25 \times 10^{-3} M$)	Tungstic acid ($1 \times 10^{-2} M$)
0 min.	0·98 c.c.	0·98 c.c.	0·98 c.c.	0.98 c.c.	0·98 c.c.
90	,,	0·96	0·97	0·97	0·98

From the above table it is clear that the blue colour of the mixtures is due to the reduction of the sols by 1 or 2 % of ascorbic acid present in the mixture.

The oxidation of ascorbic acid was determined by measurement of the oxygen consumption by the well known Warburg method. One Warburg cell contained only a little water and the reading of the manometer attached to it was subtracted from the readings of the other manometers, in order to eliminate the errors due to changes in the external conditions. The second cell contained pure ascorbic acid solution and the rest contained ascorbic acid solution with sols of different concentrations. Precautions were taken during the course of the experiment to avoid contamination of the solutions by heavy metals. Warburg cells were carefully cleaned and minimum quantity of grease was used for ground joints so that ascorbic acid solution did not come in contact with grease while shaking. Merck's extra pure hydrochloric acid, sodium meta-vanadate, sodium molybdate, sodium tungstate, caustic soda and Light's purest synthetic *l*-ascorbic acid were used throughout the investigation. For making solutions redistilled water was used.

The experiments were carried out at temperatures between 24° and 32° and at pH range 3·5 to 4·3. Each experiment was conducted for 90 minutes and manometer readings were taken at intervals of 30 minutes.

The experimental results are given in Figs. 1—7. Results obtained with vanadic acid sol are illustrated in Figs. 1, 2 and 3. Results obtained with molybdic acid sol are illustrated in Figs. 4, 5 and 6. Fig. 7 gives the results with tungstic acid sol. In Figs. 1 - 7, volume of solution = 2c.c., number of oscillations per min. = 120, air = 17c.c. and amplitude = 8 cm.

FIG 1.
Vanadic acid sol,
Temp = 30°. pH = 4·3, Ascorbic acid = $1 \times 10^{-2} M$.

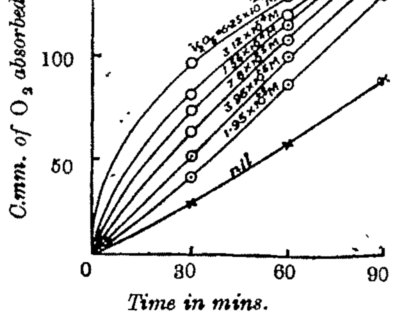
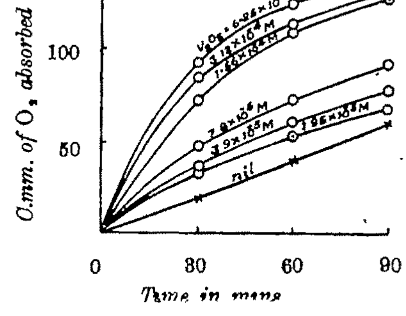


FIG. 2.
Vanadic acid sol.
Temp. = 32°. pH = 3·7. Ascorbic acid = $1 \times 10^{-2} M$.



From Fig. 1, it will be seen that at pH 4·3 the rate of oxidation of ascorbic acid ($1\times10^{-2}M$) increases as the concentration of the sol increases from $1{\cdot}95\times10^{-5}M$ to $6{\cdot}25\times10^{-4}M$ and when the concentration of the sol is increased more, the rate of oxidation practically remains constant. When the results in Fig. 1 are compared with the results in Fig. 3, it is evident that as the concentration of ascorbic acid is increased, keeping the concentration of the sol constant, the rate of acceleration of ascorbic acid oxidation is diminished. Curves in Fig. 2 illustrate the effect of lowering the pH of the solutious. At pH 3·7 the activity of the sol in accelerating the oxida- of ascorbic acid is found to be increased.

FIG. 3

Vanadic acid sol.

Temp. = 30°. pH = 4·3,

Ascorbic acid = $5\times10^{-3}M$.

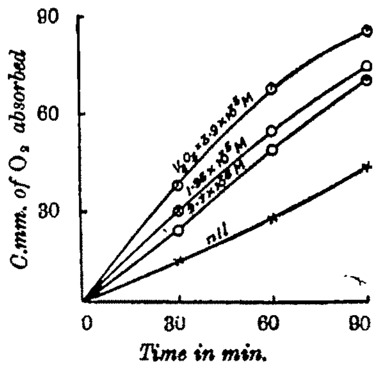


FIG. 4

Molybdic acid sol.

Temp. = 24°. pH = 4·3.

Ascorbic acid = $1\times10^{-2}M$.

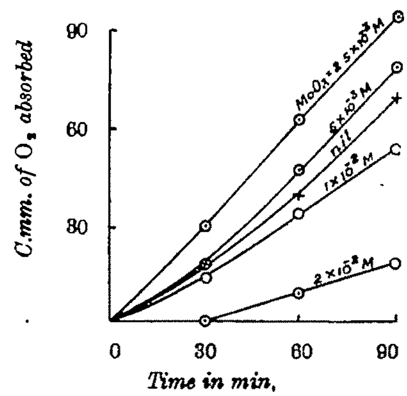


FIG. 5

Molybdic acid sol.

Temp. = 28°. pH = 4.3.

Ascorbic acid = $1\times10^{-2}M$

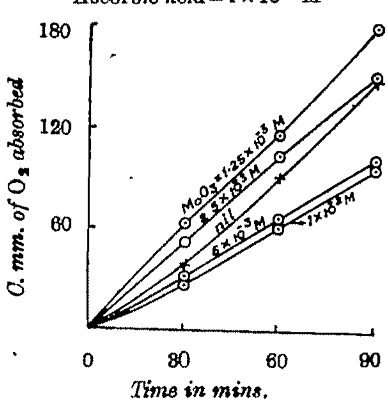
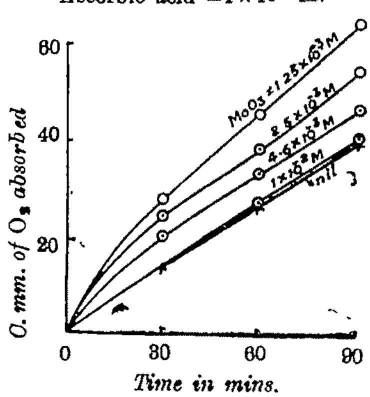


FIG. 6.

Molybdic acid sol.

Temp. = 28°. pH = 3·5.

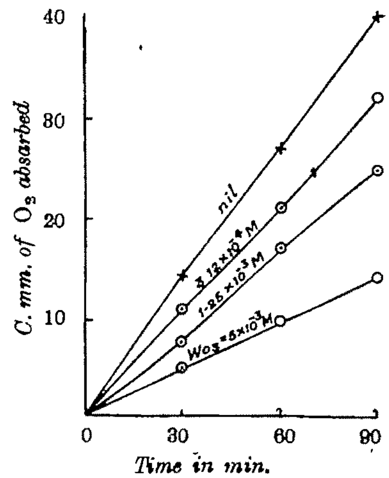
Ascorbic acid = $1\times10^{-2}M$.



Curves in Fig. 4 clearly indicate that at pH 4·3 the rate of oxidation of ascorbic acid ($1\times10^{-2}M$) increases as the concentration of the sol is decreased from $2\times10^{-2}M$ to $2{\cdot}5\times10^{-3}M$ and when the concentration of the sol is decreased more, the rate of oxidation remains constant. The effect of increasing the concentration

of ascorbic acid keeping the concentration of the sol constant (Figs. 4 & 5) and the effect of lowering the *p*H of the solutions (Fig. 6) are practically the same as in the case of vanadic acid sol.

FIG. 7.
Tungstic acid sol.
Temp. = 28°. *p*H = 8·5
Ascorbic acid = $1 \times 10^{-2} M$



At *p*H 3·5 tungstic acid in all concentrations inhibits the auto-oxidation of ascorbic acid and the rate of oxidation of ascorbic acid in presence of the sol increases as the concentration of the sol diminishes (Fig. 7).

My best thanks are due to Sir J. C. Ghosh for his kind interest and to Dr. S. K. Bhattacharyya for his helpful suggestions during the course of this work.

CHEMICAL LABORATORIES,
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SPECTROCHEMICAL ANALYSIS OF COPPER AND CADMIUM IN THE PRECIPITATES OF CADMIUM AND COPPER QUINALDINATES

By. A. K. Majumdar

Following the method of Nitchie, quantitative spectral analyses of Cd and Cu, adsorbed in the precipitates of Cu and Cd respectively, have been made.

In previous communications (Majumdar, *Analyst*, 1939, **64**, 874 ; 1943, **68**, 242) it has been shown that copper can be separated from cadmium in presence of sulphuric acid by means of quinaldinic acid following the method of Rây and Bose (*Z. anal. Chem.*, 1933, **95**, 400).

Lindsay and Shenan (*Analyst*, 1940, **65**, 636), who failed to obtain a satisfactory separation by this method, showed by means of cadion that the copper precipitate always contained cadmium. Cadion, whose high sensitivity approaches one part of cadmium in 300 million parts, is, however, unsuitable for obtaining a quantitative estimate of the amount of cadmium in the copper precipitate.

With a view to obtaining a quantitative idea about the amount of cadmium and copper adsorbed in the precipitates of copper and cadmium respectively, the present spectro-analytical work was undertaken, in which the method of Nitchie (*Ind. Eng. Chem. Anal. Ed.*, 1929, **1**, 1) was followed for quantitative spectral analysis.

Experimental

The strength and the amounts of standard solutions, the procedure adopted for the precipitations, the manner of washings of the precipitates of copper and cadmium, were exactly the same as was reported in a previous paper (*Analyst*, 1943, **68**, 242) except that the precipitates were filtered through Schleicher and Schull's white-band filter paper No. 590. The precipitates were then taken in separate crucibles, decomposed to anhydrous sulphates by heating with concentrated sulphuric acid (reagent quality) and transferred into the cavities of different electrodes of purified gas carbon.

Where, according to the earlier paper already mentioned, the quantity of copper taken for analysis was 26·7 mg., the entire sulphate of copper was put in the lower positive electrode. If, however, the copper taken was double this amount, the sulphate was then made up to 50 c.c. with double distilled water, 25 c.c. of which were evaporated to dryness and the residue used for spectral analysis.

Similar procedure was also adopted in the case of cadmium. If the quantity of cadmium were 30·95 mg., the entire sulphate was taken, but if it was double or treble this amount, the sulphate was made up to a definite volume with water and half or one-third of the total volume taken for use.

For the purpose of preparing a series of standard plates, representing different percentages of cadmium in copper (*e.g.* 0·1 to 0·01), the same quantity of standard

copper sulphate solutions containing 26·7 mg. of copper was taken in several crucibles. A definite amount of dilute standard cadmium sulphate solution of concentrations varying from $26·7 \times 10^{-3}$ mg. to $26·7 \times 10^{-4}$ mg. were added to each crucible along with 15 c.c. of 1% solution of quinaldinic acid. The solution in each crucible was then converted into anhydrous sulphate as mentioned above and the entire mass was used for arcing.

In the same way standard plates from 0·1 to 0·5% of copper in cadmium, were prepared by using 30·95 mg. of cadmium sulphate solution and varying amounts of copper ($30·95 \times 10^{-3}$ mg. to $15·485 \times 10^{-2}$ mg.) from diluted standard copper sulphate solutions.

A large Littrow-type E_1-quartz spectrograph was used and the spectrum from λ 2350 to λ 3400Å, distributed over 10 inches, was photographed on Ilford Special Rapid plates. No special treatment of the plates has been found necessary.

The electrodes used were of carbon, 33 mm. long, 9 mm. in diameter and the positive rod contained a cavity 5 mm. wide and 4 mm. deep into which samples were introduced. The negatives were sharpened to fine points which helped in centering and steadying the arc.

The electrodes were purified according to the method of Staud and Ruehle (*Ind. Eng. Chem. Anal. Ed.*, 1938, **10**, 59) and prior to adding the sample, they were burnt for 30 seconds in 10·5 ampere arc to eliminate any remaining impurities.

A quartz condensing lens was used to concentrate the light from the arc on the slit. Suitable adjustments were made permitting the arc to be moved both horizontally and vertically, so as to keep it properly centred.

The tips of the electrodes were kept, as far as possible, at a constant distance from each other to maintain current and voltage drop constant, and the image of the arc properly centred on the slit aperture.

For each sample, a three-minute exposure was given with a current of $10·5 \pm 0·5$ amperes. The time was sufficient for the complete vaporisation of the samples.

RESULTS

Lines used for comparison in the case of cadmium arc were λ3403·8 and λ 3261·2Å.

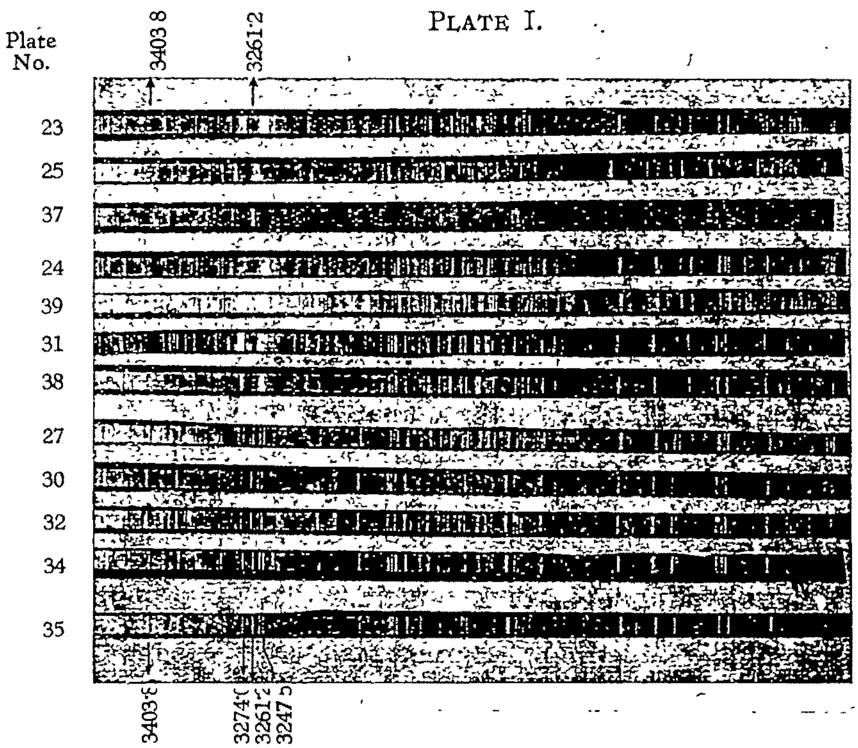
TABLE I

Metals taken.	2N-H_2SO_4.	Regent added (quinaldinic acid 1% neutralised by Na_2CO_3)	Cd in Cu ppt.	Cu in Cd ppt.	Plate No. for Cd in Cu.	Plate No. for Cu in Cd.
Cu, 26·7 mg. Cd, 30·95	2 c.c.	30 c.c.	0·06%	0·3%	24	27
Cu, 26·7 Cd, 61·9	5	30	0·07	0·3	39	30
Cu, 26·7 Cd, 92·85	2	30	0·06	0·3	31	32
Cu, 53·4 Cd, 30·95	10	60	0·05	0·3	38	34

Standard plates for cadmium in copper are Nos. 23, 25 and 37 containing respectively 0·1%, 0·07% and 0·04% of cadmium (Plate I).

In developing the plates, the concentration of the developer, the time for developing and fixing were maintained constant for every plate. It may be seen that the copper precipitate contains only 0·05 to 0·07% cadmium. On the other hand, the cadmium precipitate shows a comparatively large amount—about 0·3% of copper in it. In any case, the adsorption of cadmium in copper or of copper in cadmium is not likely to affect to any material extent the results of quantitative separation of copper from cadmium by the quinaldinic acid method, as already established in previous communications.

PLATE I.



My best thanks are due to Prof. P. Rây and Dr. J. Gupta for their kind interest in the work.

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ORTHO-SUBSTITUTED DIPHENYLS

By S. H. Zaheer and S. A. Faseeh

2-Chloro-, -bromo-, -iodo- and -cyano-diphenyls as well as the magnesium compound of 2-iodo-diphenyl have been prepared. A method for the preparation of the magnesium compound of 2-chlorodiphenyl has been described.

Mono-*ortho*-substituted diphenyl halides can form the starting material for the synthesis of a number of *ortho*-substituted diphenyls, whose preparation has so far either not been attempted at all or is possible only through tedious methods giving poor yields. While there are a number of references available for the method of preparation of 2-iododiphenyl (Gilman and others, *J. Amer. Chem. Soc.*, 1929, **51**,2260 ; Mascarelli and others, *Chem. Zentrl.*, 1932, II, 2713) there are only meagre data existing for the preparation of 2-bromo-and 2-chloro-diphenyl (Mascarelli, *loc. cit.*). Using 2-aminodiphenyl as the parent substance these compounds have been prepared by the Sandmeyer's reaction in satisfactory yields.

Of the three *o*-substituted diphenyl halides, only the iodide reacts readily with magnesium to give the Grignard reagent under usual conditions. Owing to the liberation of large quantities of iodine the use of magnesium derivative of *o*-iodo-diphenyl for the synthesis of other *ortho*-substituted derivatives of diphenyl by the Grignard reaction is inconvenient. Attempts to prepare by the usual method the magnesium compounds of the corresponding bromo and chloro derivatives have, however, been unsuccessful.

A good yield of the magnesium derivative of 2-chlorodiphenyl has, however, been obtained by heating together magnesium flakes with 2-chlorodiphenyl in an evacuated and sealed hard glass tube at 210-215°.

Experimental

2-*Chlorodiphenyl.*—A solution of 2-aminodiphenyl (21g.) in 10 c. c. hydrochloric acid (1 : 1) was diazotized by sodium nitrite solution (10g. in 20 c. c. water). The solution was added to a freshly prepared cuprous chloride solution, prepared from 18g. of copper sulphate. When the evolution of nitrogen ceased, the solution was made alkaline with sodium hydroxide and distilled in steam. The distillate was extracted with ether and the ether extract dried and after removal of ether the product was distilled at 154°/12·5 mm., yield 24g. (60%). $D_{32 \cdot 5}$, 1·1499. It solidifies to colourless crystals, m. p. 31°. (Found : C, 76·52 ; H,4·81 ; Cl, 18·88. $C_{12}H_9Cl$ requires C,76·49 ; H,4·77 ; Cl, 18·83 per cent).

2-*Bromodiphenyl.*—A solution of 2-aminodiphenyl (21g.) was diazotized and treated with cuprous bromide solution, prepared from 16 of copper sulphate. The product was isolated as in the previous case and a yellow oil obtained, b.p. 160°/11 mm.

D_{26}, 1·2175, yield 18·7g. (65%). (Found : Br, 34·15·. $C_{12}H_9Br$ requires Br, 34·30. per cent).

2-Iododiphenyl.—A solution of 2-aminodiphenyl (21g.) was diazotized and treated with a solution of potassium iodide (30g. in 300 c c. water). The iodo compound was isolated as usual. A light yellow oil, b. p. 181°/21 mm, yield 24·3g (70%). $D_{27\cdot3}$, 1·6031. (Found : I, 45·51. Calc for $C_{12}H_9I$: I,45·34 per cent).

2-Cyanodiphenyl.—A solution of 2-aminodiphenyl (20g) was diazotized and the solution treated with cuprous cyanide solution prepared from 35 g. of copper sulphate. When evolution of nitrogen ceased the solution was warmed for half an hour on a water-bath, made alkaline with sodium hydroxide and then distilled in steam. The distillate was first shaken with stannous chloride solution to remove any yellow azo-dye formed and then the tin was precipitated with sodium hydroxide solution. It was then extracted with ether and the ether extract dried and distilled. It was obtained as a yellow oil, b. p. 174°/13 mm., yield 11·0 g (50·%). On keeping it in a referigerator for a week the oily liquid crystallised to faintly coloured needle shaped crystals, m. p. 37°. (Found : C,87·18 ; H, 5·0 ; N, 7·68. Calc. for $C_{13}H_9N$: C, 87·14 ; H, 5·03 ; N, 7·82 per cent). 2-Cyanodiphenyl was prepared by Knorr (*Annalen*, 1928, **464**, 34) and also by Braun (*ibid.*, 1929,**468**, 273).

Magnesium derivative of 2-Iododiphenyl.—A solution of 2-iododiphenyl (7·0g.) in absolute ether (70 c. c.) and magnisium flake (0·7g.) was refluxed with stirring in an inert atmosphere of hydrogen for about 2 hours. After the reaction was complete, the quantity of magnesium compound formed was determined. The solution was made up to 100 c. c. with absolute ether. 10 C. c. of this solution were hydrolysed by boiling with 150 c. c. of water and 20 c. c. standard sulphuric acid. The excess of acid was titrated against standard sodium hydroxide according to the method described by Gilman and Meyer (*J. Amer. Chem. Soc.*, 1923, **45**, 159). The quantity of magnesium compound is about 80% of the theory.

Magnesium derivative of 2-Chlorodiphenyl.—Magnesium flakes (0·8 g.) and 2-chlorodiphenyl (5 g.) were heated together in an evacuated and sealed hard glass tube (1·0 cm. bore) for 6 hours in an air-bath at 210-15°. After the reaction was complete, the contents of the tube were dissolved in 100 c.c. of absolute ether and the percentage yield determined as in the previous case. yield 32% of theory.

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RHEOCHOR AND ITS APPLICATION

By W. V. Bhagwat, P. M. Toshniwal and V. A. Moghe

The suggestion of Newton Friend to use viscosity for finding rheochors has been investigated and atomic rheochors calculated. It is shown that the values give fairly accurate results with rheochors of substances obtained experimentally. The suggestion has been extended to solutions and shown to be applicable to cane sugar solution.

Newton Friend (*Nature*, 1942, **140**, 432) suggested that in Sudgen's parachor $\sigma^{\frac{1}{4}}$ may be substituted by $\eta^{\frac{1}{8}}$, where σ and η are surface tension and viscosity respectively of the liquid. This gives

$$\frac{M\eta^{\frac{1}{8}}}{D} = \text{Constant} = R$$

where M is the molecular weight and D, the density of the liquid. The name *Rheochor* is suggested for this constant. Friend observes that isomerides yield identical values of R. However, he has published no data as regards atomic rheochors and their application.

We have tried to use this formula for calculating rheochors of several liquids and thus calculated the values of atomic rheochors. The values of D and η in the following table are obtained from the Chemist's Year Book (1937) and are at 20°.

Table I

Liquid.	$\eta \times 100$.	D.	R.	Group diff.	Diff. of R.
C_6H_6	0·65	0·879	47·28	CH_2	7·45
$C_6H_5{\cdot}CH_3$	0·59	0·864	54·73	CH_2	10·0
m-$C_6H_4(CH_3)_2$	0·61	0·864	64·72		
CH_3OH	0·59	0·790	21·33	CH_2	12·16
C_2H_5OH	1·19	0·789	33·49	$2(CH_2)$	2(8·035)
$(C_2H_5)_2O$	0·23	0·715	49·56		
$(CH_3)_2CO$	0·33	0·792	35·83		
CH_3COOH	1·22	1·054	32·82		
$CHCl_3$	0·56	1·488	41·89		
CCl_4	0·97	1·582	54·58		
CS_2	0·37	1·292	29·0		
CO_2 (liquid)	0·07	0·83	21·89		
Br_2	0·99	3·187	13·8		
Hg	1·56	13·59	8·75		
n-C_6H_{14}	0·32	0·660	63·55		
$C_6H_5NH_2$	0·44	1·018	46·36		

Having failed to obtain a constant value for CH_2 group we determined the rheochors of the members of homologous series available in our laboratory. Following are the results.

TABLE II

Liquid.		$\eta \times 100$.	*D.*	Temp.	*R.*	Group dift.	*R.* diff.
Methyl alcohol	...	0·59	0·790	20°	21·33	CH_2	12·16
Ethyl alcohol	...	1·19	0·789	,,	33·49		
		1·047	0·785	25°	33·18	CH_2	12·0
Propyl alcohol	...	1·851	0·8078	,,	45·12		
Amyl alcohol	...	2·900	0·8052	,,	70·21	2 (CH_2)	2 (12·55)
Acetic acid	...	1·22	1·054	20°	32·32		
Butyric acid	...	1·677	0·9528	25°	55·42	2 (CH_2)	2 (11·3)
Ethyl formate	...	0·424	0·9099	25°	41·09	CH_2	9·12
Ethyl acetate	...	0·436	0·888	,,	50·21		
Ethyl butyrate	...	0·6033	0·867	,,	70·64	2 (CH_2)	2 (10·21)
Acetone	...	0·33	0·792	20°	35·83	CH_2	9·7
Methylethyl ketone	...	0·45	0·805	25°	45·53		

The values of CH_2 group for associated liquids as alcohols and acids are somewhat high. Average value of rheochor of CH_2 is 10, and the values of atomic rheochors calculated with this value gives better results than any other value of CH_2 group. Substituting this value for the rheochor of CH_2 in hexane, ethyl ether, and other compounds we get the following values of atomic rheochors.

TABLE III

Element.		*R.*	Element.	*R.*
Hydrogen	...	1·77	Chlorine	11·6 (average)
Carbon	...	6·44	Bromine	13·8
Oxygen	...	6·02	Mercury	8·75
Sulphur	...	11·28		

These values of atomic rheochors, when substituted in various compounds, reproduce the rheochors of the compounds fairly accurately although alcohols and aromatic hydrocarbons show marked deviation. In case of alcohols and acids the variation is partly due to the different values of hydroxyl and carboxyl oxygen than the value given in table which is for rheochor of ethereal oxygen and partly, due to the difference in the calculated and observed value for alcohols is not being the same although they contain the same number of atoms of hydroxyl oxygen. Similarly the variation of rheochors of aromatic hydrocarbons from experimental values is not constant although each contain only one benzene ring. It is not possible therefore to calculate rheochor for a ring of six. The variation is also not due to incorrect values of C and H rheochors, for the difference of rheochors from member to member is not very constant and that when the value of CH_2 from alcohols or aromatic hydrocarbons is substituted in other compounds, we get wrong results for rheochors of these compounds. Any how it is not possible to explain the discrepancy at this stage and the

values of atomic rheochor given above have to be taken as fairly accurate. Further work is in progress. The following table gives our results.

TABLE IV

Substance.		R obs.	R calc.	Substance.		R obs.	R calc.
n-Hexane	...	63·55	63·55	Benzene	...	47·28	49·26
Ethyl ether	...	49·56	49·57	Toluene	...	54·73	59·26
Carbon tetrachloride	...	54·58	53·24	*m*-Xylene	...	64·72	69·26
Carbon bisulphide	...	29·0	29·0	Acetic acid	...	32·82	32·0
Chloroform	...	41·89	43·0	Butyric acid	...	55·42	52·0
Acetone	...	35·83	36·0	Methyl alcohol	...	21·38	19·54
Methylethyl ketone	...	45·58	46·0	Ethyl alcohol	...	33·13	29·54
Ethyl formate	...	41·09	42·0	Propyl alcohol	..	45·12	39·54
Ethyl acetate	...	50·21	52·0	Amyl alcohol	...	70·21	59·54
Ethyl butyrate	...	70·64	72·0	Carbon dioxide (liquid)		21·89	18·44
Water	...	10·0	9·5				

We suggest that like parachor, rheochor can be detetmined by the solution method both from liquids and solids by the expression,

$$R_m = R\ (1-x)+x.\ R_x.$$

where R_m is the rheochor of the solution, R of the solvent and R_x of the solute whose molecular fraction in solution is x. R_m is given by the expression,

$$R_m = \frac{M_m\ \eta^{\frac{1}{8}}}{D}$$

where M_m = the mean molecular weight of the solution,

η = the viscosity of the solution,

D = the density of the solution.

M_m is obtained from the equation $M = M\ (1-x)+x.\ M_x$
where M and M_x are the molecular weights of solvent and solute respectively.

Our suggestion is somewhat confirmed in case of cane sugar dissolved in water. The results of η and D in Table V are obtained from Chemist's Year Book, 1937.

TABLE V

R for water = 10·26. Temp. = 30°.

x	M_m	η.	D	R_m.	R_x.
0·01299	22·2	2·267	1·083	12·77	204
0·03390	28·99	7·468	1·179	17·78	230

Calculated value for R_x with $CH_2 = 10$ is 182·5, while with $CH_2 = 12$ as in alcohols it is appproximately 210. If we take $H_2O = 10·26$ and $C = 6·44$, we get $R_x = 190$. It is clear therefore that solution law seems to be applicable. Further work is in progress to get more accurate values of atomic rheochors from various substances.

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ON THE CONSTITUTION OF THE TANNIN FROM INDIAN TERIPODS

By H. G. Biswas

From the pod cases of *Caesalpinia digyna* a tannin (m.p 200 - 12°) has been isolated (acetyl derivative, a colourless crystalline solid, m p. 206° - 208° decomp). From the analytical data and study of hydrolysis the tannin has been proved to be a monodigalloyl glucose.

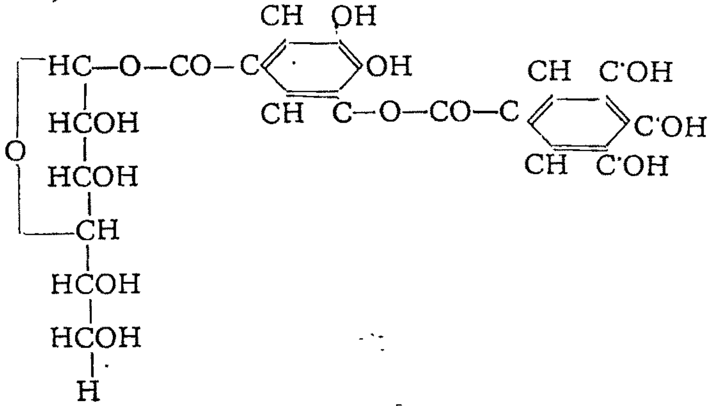
Caesalpinia digyna grows in the Eastern and Western peninsula, Assam, Bengal, Burma, Sambalpur, Ceylon and Eastern Himalayas. It is a large woody shrub. The pods are oblong, turgid, glabrous and $1\frac{1}{2}-2''$ in length, containing 2 to 4 pea-like seeds. The pod cases contain a tannin, very suitable for making writing ink.

Teripods are known to contain an appreciable amount of tannin (Kirtikar and Basu, "Indian Medicinal Plants", p. 466).

Nierenstein remarks ("The Natural Organic Tannis", 1934, p. 194) "According to Dekker, divi-divi-tannin is probably identical with algarobillitannin; and this probably also applies to the tannin present in teri-pods (*Caesalpinia digyna*)".

The outer skin of the ripe pods contains a red colouring matter and when extracted with the usual solvents it comes along with the tannin and it becomes very difficult to remove it in subsequent operations. It has been found, however, that by careful scraping off of the skin of the ripe dry pods or by using dry unripe pods, the tannin can be obtained colourless. It has been found by the author that divi-divi-tannin is quite different from the teripod tannin. The tannin is hydrolysed according to the method of Fischer and Freudenberg (*Ber.*, 1912, **45**, 915) and 65% gallic acid are obtained (calculated for monodigalloyl glucose it would be 70·2%). The reducing sugar has been proved to be glucose (25%, monodigalloyl glucose would yield 37·1% glucose). The small yield of sugar may be attributed to the partial decomposition of it by sulphuric acid during hydrolysis. The acetyl derivative (m.p. 206-208°) has been prepared with acetic anhydride and pyridine in the cold (Fischer and Bergmann, *Ber.*, 1918, **51**, 1797).

The results of hydrolysis and the analytical data for the tannin as well as for its acetyl derivative are in fair agreement with monodigalloyl glucose. Hence teripod tannin should have the formula $C_6H_{11}O_5-O-COC_{13}H_9O_7$, and it may be structurally represented as follows from analogy to glucogallin (Fischer and Bergmann, *loc. cit.*).



EXPERIMENTAL

Isolation of the Tannin.—Dry ripe teripods, the reddish skin of which was carefully scraped off, were powdered, seeds removed and extracted with absolute alcohol in a Soxhlet. The alcohol was completely removed from the extract on a water-bath and the residue dissolved in water (charcoal). The aqueous solution was evaporated to dryness in vacuum, yield 40 g. (from 95 g. of powdered teripods). The crude tannin was dissolved in a little water, made slightly alkaline to litmus with sodium bicarbonate and then thoroughly extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried over anhydrous sodium sulphate and the ethyl acetate was removed. The residue was again dissolved in a little water (charcoal) and the solution evaporated to dryness in *vacuo.* The colourless substance was powdered, dried in a steam bath and vacuum desiccator for several days. It melts with decomposition at 205-12°. It shows every characteristic reaction of tannic acid. (Found : C, 48·86 ; H, 4·58. $C_{20}H_{20}O_{14}$ requires C, 49·5 ; H 4·13 per cent).

Hydrolysis of the Tannin.—A solution of the tannin (5 g.) in sulphuric acid (5%, 250 c.c.) was heated on the water-bath for 30 hours. The solution on allowing to stand for a few days was treated with just sufficient quantity of baryta to remove H_2SO_4, the filtrate extracted several times with ethyl acetate till ferric chloride gave but a very faint colouration. The ethyl acetate extract was shaken with sodium chloride and then the solvent was completely removed. A brownish crystalline substance was obtained, yield 3·2 g. which crystallised from water, m.p. 224-26° (mixed m.p. with gallic acid). It gives pyrogallol on heating.

The sugar was isolated according to the method of Fischer and Freudenberg (*loc. cit.* 1912). To the mother-liquor obtained after removing gallic acid with ethyl acetate, lead carbonate (0·5 g.) was added, the solution boiled for 15 minutes, then in the hot, alternately a small amount of hot concentrated aqueous solution of monobasic lead acetate and lead carbonate added till it was neutral to litmus. CO_2 was passed through the solution till it was cold and filtered. The filtrate was warmed, H_2S passed into the solution and filtered. The filtrate was boiled to remove H_2S completely. The solution was concentrated in *vacuo* on a water-bath and left to stand for several days when crystals (1·2 g.) separated. It reduced Fehlings solution. A portion on recrystallisation melted at 140-42°. The osazone, prepared in the usual way, melted at 200°. The sugar is therefore glucose.

Acetylation.—Teripod tannin (1 g.) was gradually added to a mixture of 4 c. c. of acetic anhydride and 4 c.c. of dry pyridine ; during addition it became warm so it was cooled and then left to stand at room temperature for 3 days. On pouring into ice-cold dilute sulphuric acid an oil separated which solidified on keeping overnight. It was collected, washed with water and dried in a vacuum desiccator. It was then dissolved in 5 c.c. of dry chloroform and on pouring it into 50 c.c. of dry methyl alcohol, cooled in a freezing mixture, white crystalline precipitate appeared. It was quickly filtered and dried in a vacuum desiccator. The acetyl derivative is a microcrystalline colourless substance, m.p. 206-8° (decomp.). An acetone solution of it

colouration with ferric chloride and it is insoluble in water. [Found : C, 55·0 ; H, 4·3. $C_{20}H_{11}O_{13}(CH_3CO)_9$ requires C, 55·5 ; H, 4·44 per cent].

My sincere thanks are due to Mr. S. J. Das-Gupta for his kind criticism and to the authorities of the firm for the facilities offered.

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CONDENSATION OF 3 : 5-DINITRO-4-CHLOROBENZALDEHYDE WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES

BY D. S. MITTAL

3 : 5-Dinitro-4-chlorobenzaldehyde (Mittal, *J. Indian Chem. Soc.* 1942, **19**, 408) has been condensed with malonic acid using various organic bases and it has been found that the condensation takes place smoothly and the yield is almost quantitative when for one molecule of the aldehyde only one of the acid and 0·15—0·25 mol. of pyridine or a similar base are used, as has been previously observed in other cases (*cf.* Mittal, *J. Indian Chem. Soc.*, 1942, **19**, 47).

The condensations were carried out exactly following the method of Pandya (*J. Indian Chem. Soc.*, 1934, **11**, 824. *et seq.*).

Catalyst.	Amount of catalyst.	Yields	
Pyridine	0·15 mol.	1·09 g.	92·87%
Piperidine	,,	1·06	88·98
Quinoline	,,	1·00	84·74
Without base	,,	0·59	50·00

This cinnamic acid was recrystallised from alcohol as yellow needles, m.p. 82°. (Found : N, 10·40 ; Cl, 12·85. $C_9H_5O_6N_2Cl$ requires N, 10·27 ; Cl, 13·02 per cent).

The author's thanks are due to Dr. S. M. Sane for the guidance during the course of the work and to the authorities of the Lucknow University for the facilities offered for research.

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ON THE FATTY ACIDS OF MARGOSA (NEEM) OIL

By Reginald Child and Wilfred R. N. Nathanael

The existence of a specific "margosic" acid, $C_{22}H_{40}O_2$, in margosa oil, claimed by Chatterjee and Sen (*Indian J. Med. Res.*, 1920-21, 8, 56) may be regarded as satisfactorily disproved by subsequent workers, although references to "margosic" acid still sometimes occur in medical literature in connection with its supposed value in the treatment of leprosy. Roy and Dutt (*J. Soc. Chem. Ind.*, 1929, **48**, 333T), Child and Ramanathan (*ibid.*, 1936 **55**, 124T) and Hilditch and Murti (*ibid.*, 1939, **58**, 310T) agree that palmitic, stearic, oleic and linoleic acids account for the bulk of the component fatty acids, whilst the last two authors have further demonstrated the general make-up of the glycerides constituted from these four acids.

It is surprising that Qudrat-i-Khuda *et al.* (*J. Indian Chem. Soc.*, 1940, **17**, 189) have entered this field with a claim to have demonstrated the existence of four entirely new fatty acids, whose glycerides they say make up the bulk of margosa oil. "Earlier workers", they opine, "were misled by the physical properties of the acids because we do not find any analytical data regarding the acids from the papers of these aurhors".

This criticism can hardly be taken seriously. Chatterjee and Sen (*loc. cit.*) though mistaken over "margosic" acid, were satisfied that stearic and oleic acids were major components of the oil. Roy and Dutt (*loc. cit.*) separated their "solid" and "liquid" acids by rather crude methods, and certainly under-estimated the content of linoleic acid, but they did quite adequately identify the acids present. Palmitic and stearic acids were separated from the "solid" acid by the method of Hehner and Mitchell; the presence of a small perentage (0·74) of higher saturated acid was clearly shown; oleic acid was identified by conversion into elaidic acid (m. p. 42-3°, M. W. by analysis of silver salt, 283) and by oxidation to 9 : 10-dihydroxystearic acid, m. p. 133°; linoleic acid was identified by oxidation to tetrahydroxystearic acid, m.p. 163-65°.

Child and Ramanathan, by lead salt separation and ester fractionation, accounted for 97·6% of the total acids obtained by saponification of margosa oil. They recorded their analytical data in full, comprising saponification equivalents and iodine values of twelve "solid" ester fractions, and S.E.'s, I.V's and thiocyanogen values of six "liquid" ester fractions.

It should not be necessary to re-discuss the principles underlying the ester fractionation technique. These have been adequately established by Armstrong, Allen and Moore (*J. Soc. Chem. Ind.*, 1925, **44**, 63T) and by Hilditch (*cf. Biochem. J.*, 1934, **28**, 779; "The Chemical Constitution of Natural Fats", 1940, Chapter XI), and a moderate acquaintance with the progress of fat chemistry in recent years is sufficient to show that they have justified themselves in practice. With the work of Roy and Dutt behind them and the range of their analytical data being obviously

normal, it would have been a work of supererogation for Child and Ramanathan to recover and identify the acids from their ester fractions.

However, by good fortune, the "solid" ester fractions from the work of Child and Ramanathan had been retained in this laboratory, and the present authors have had no difficulty in isolating from suitable fractions pure palmitic and stearic acids. "Liquid" fractions had not been retained, but a fresh sample of "liquid" acids was prepared from a sample of margosa oil of similar origin to that investigated in 1935. From these oleic acid was isolated semi-quantitatively as the characteristic lithium salt and converted into 9 : 10-dihydroxystearic acid. Linoleic acid was identified similarly as terahydroxystearic acid.

When this work was nearly completed there appeared a paper by Dasa Rao and Seshadari (*Proc. Indian Acad. Sci.*, 1942, **15A**, 161), whom we thank for sending us a copy of their publication. These authors report a fractionation analysis on a sample of margosa oil from the Ramnad district, Andhra Province, S. India, and give figures which accord very closely with those of Child and Ramanathan (see Table I). We agree with them in supporting the suggestion of Hilditch and Murti that differences in recorded analyses may be due to climatic or varietal differences; as they point out, the climate of the Ramnad district is not very different from that of the Trincomalee district of Ceylon, whence we obtained our material. It may be noted, too, that recorded variations are consistent with the differences in iodine values (see Table I), if we neglect the figures of Roy and Dutt, who, as stated above, obviously under-estimated linoleic acid.

TABLE I

Component acids of margosa oil.

(Percentage by weight, excluding unsaponifiable matter)

	Roy & Dutt.	Child & Ramanathan.	Hilditch & Murti.	Dasa Rao & Seshadri.
	1929.	1936.	1939.	1942.
Palmitic	14·2	13·6	14·9	13·8
Stearic	24·1	19·1	14·4	18·2
Arachidic	0·8	2·4	1·3	1·8
Oleic	58·6	49·1	61·9	52·6
Linoleic	2·3	15·8	7·5	13·6
Iodine value	...	71·5	67·9	69·2
Origin of sample	...	Trincomalee, Ceylon.	Cawnpore, U. P. India.	Ramnad district, Andhra Prov. S. India.

Dasa Rao and Seshadri repeated the work of Qudrat-i-Khuda *et al.* and showed quite clearly that all the so-called "new acids" of the latter authors are

mixtures, the "A" and "B" acids containing mostly palmitic and stearic (with arachidic) acids ; and their oil "X", from which were "isolated" Qudrat-i- Khuda's unsaturated acids "C" and "D", being a heterogeneous mixture still containing considerable amounts of saturated acids.

We are, with Dasa Rao and Seshadri, completely satisfied that the so-called new acids of Qudrat-i-Khuda and his colleagues are nothing more than mixtures of known acids, and that from their methods of separation nothing else could have been expected. It is not our business to account for their curious molecular weight figures for acids "A" and "C". It is sufficient to say that three separate sets of workers have now recorded ester fractionation analyses and in no case has a methyl ester fraction been obtained of a molecular weight below 270 (methyl palmitate). Ester fractionation technique would certainly have revealed as little as 2% of any acid of lower molecular weight than palmitic, had it been present. Qudrat-i- Khuda's reasons for supposing his acid "B" $C_{16}H_{32}O_2$, m.p. 55°, to be an "isomer" of palmitic acid, appear to us unconvincing as also his ascription of acid "D", $C_{18}H_{32}O_2$ to the cyclic series.

The history of fat chemistry is littered with "new" fatty acids, few of which have survived critical study. Margosa oil adds a curious chapter to this history, from Chatteriee and Sen's "margosic" acid, $C_{22}H_{40}O_2$ to Qudrat-i-Khuda's four "new" acids, $C_{14}H_{28}O_2$ and $C_{16}H_{32}O_2$, $C_{15}H_{28}O_2$ and $C_{18}H_{32}O_2$. We perhaps need hardly comment on the *a priori* improbability of the existence of the C_{15}-acid.

COCONUT RESEARCH SCHEME,
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A NOTE ON PURE CHARCOAL FROM CANE SUGAR

By T. M. Oza

Pure sugar charcoal is prepared by the method of King (*J. Chem. Soc.*, 1933, 843). It is found that a heating to 1000° or more is not necessary at any stage during the preparation and that a temperature of 500-550° is quite enough.

Charcoal was prepared from cane sugar by Shah (*ibid.*, 1929, 2664) for combustion in oxygen and oxides of nitrogen. His charcoal is reported to leave 0·12% ash on incineration. King (*loc. cit.*) has extended this method and obtained charcoal from centrifuged coffee-sugar which leaves no ash on incineration. The present author has applied the King's method of removing mineral matter to sugar charcoal, prepared by Shah's method, and found that the comparatively large amount of mineral matter (0·75% ash) in his charcoal is mostly eliminated in only one and completely eliminated in two of King's subsequent operations.

Large crystals of cane sugar were heated in a porcelain dish (Shah, *loc. cit.*) till the charcoal formed was brittle between fingers. This charcoal (about 50 g. each time) was then heated at 500° for 7 hours, in a hyvac vacuum, in a vertical tube provided with a ground glass joint and a tap at its top, the heating of the tube and pumping of the sweet smelling gases, again generated, being continued for more than two hours at a stretch ; during the halt the charcoal was not allowed to be exposed to air. The charcoal was next heated in a current of chlorine at 500° (10 litres for 25 g.) after which it was again exhausted at 500° for two hours*. This charcoal contained adsorbed chlorine and on being incinerated gave the following results :

I. 1·3280 g. charcoal left 0·0102 g. ash (0·77 %).

II. 0·2386 g. charcoal left 0·0018 g. ash (0·75%).

Through a layer of charcoal, thus obtained, hydrogen was passed for one hour at room temperature and then for one hour at 500°. It was then finely ground and treated in a platinum vessel with hydrofluoric acid to form a paste and digested on a small flame for half an hour, the treatment with hydrofluoric acid repeated, the charcoal dried and strongly heated and thrown into pure concentrated HCl and boiled for about one hour. After diluting with much water the contents of the beaker were filtered, the charcoal washed free of chloride, dried and exhausted at 500°. On incineration 0·8667 g. charcoal left 0·0006g. ash (i.e., 0·07%). Another treatment with HF etc. eliminated the mineral matter completely (two places of decimal).

The use of ash-free charcoal in finer studies with charcoal has been emphasised by Miller (*J. Amer. Chem. Soc.*, 1922, 44, 1866). The author in his study on the action of charcoal on sodium nitrite in *vacuo* found that the charcoal before chlorine treatment reacted only violently at 265° and that the purer charcoal reacted at and above 300°, the reaction becoming violent only between 355° and 370° depending upon the purity of charcoal. The purer the charcoal, the slower was its reaction and the better was its reducing power.

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*This in Shah's method, is followed by treatment with nitric oxide and exhaustion at 1000°.

REVIEWS

Experimental Physical Chemistry.—By W. G. Palmer. Published by Cambridge University Press, 1941. Pp. 324+xii. Price 12/-sh.

In presenting this book on Experimental Physical Chemistry the author has fully kept in view the practical aspect of the subject with respect to time and laboratory facilities. A student in his practical class has to finish his course within a specified period of time and the laboratory facilities available are also limited. But the experiments discussed in this book, while covering a fairly wide ground on the experimental side of the different aspects of physical chemistry, are of such type as to impress upon the student both the theory and the technique of the general physico-chemical works. Experiments are mostly presented in a lucid manner with the underlying theory at the introduction of each chapter. Although the theoretical discussions have been brief in many cases they are after all adequate and lucid. "The apparatus is simple enough" and the students themselves can construct or assemble them from common laboratory equipments. It is particularly the simplicity of the apparatus and the practical way in which each experiment is approached where the originality of the book is to be found. Detailed instructions of the procedure and completely worked examples based upon data obtained in the laboratory are included which are sometimes helpful in economising time. While the book may be regarded as fairly comprehensive, the optical experiments and and experiments of advanced type are not included, which makes the book helpful only to the beginners. Considering the difficulties associated with the incidence of war the get-up of the book is excellent and the paper sufficiently good.

S. N.M.

Hydrogen Ions : Their Determination and Importance in Pure and Industrial Chemistry—By H. T. S Britton. Third Edition, 1942, in two volumes. Published by Chapman and Hall. Pp. (Vol I 420+xix ; Vol II. 443+xix). Price 30/-sh.

The book requires no new introduction to workers in Physical Chemistry. It has been one of the standard works on hydrogen ions since its first publication in 1929. The third edition of the book will be welcome to all workers in Physical Chemistry. The literature and the field of application of p_H are steadily growing not only in regard to chemistry but also in regard to the multifarious industries where it has found application. Frequent new editions of books on such important and progressive subjects are always helpful in obtaining a comprehensive view of the literature collected at one place. . The book has been presented in two volumes, the second volume dealing only with the industrial applications of hydrogen ions. This has reduced the bulk of the book to convenient size. In Vol. I the important features are the chapters on the Activity concept of electrolytes, rewritten, to throw more forcibly into relief the impact "which the modern theory is making on the

computation and interpretation of pH values", the chapter on the concept of Acids and Bases as enunciated by Lowry and Brönsted, which has been put as a separate chapter in the present edition and the chapter on the Polybasic Acids, which has been treated in a very comprehensive manner. In Vol. II the chapter on Oxidation-reduction processes has been considerably enlarged. However, one significant fact that stands out most unfortunately is that although the book is in many respects an improvement on the earlier editions, the references given in many cases do not usually relate to literature appearing after 1935 or 1936. Thus in the chapter, where soil fertility has been presented, the references relate to papers appearing up to 1936, although a considerable amount of work has been done in the line quite recently. We hope that this will be rectified in subsequent editions which such a popular book will certainly have. The get-up of the book is nice and the paper and binding very excellent.

S. N. M.

Diffusion in and through Solids.—BY RICHARD M. BARRER. PUBLISHED BY CAMBRIDGE UNIVERSITY PRESS, 1941. Pp. 464+xiv. Price 30/sh.

The phenomenon of diffusion finds application in many problems in physics and chemistry. Its importace in chemical kinetics, adsorption, solution, osmosis etc. are well known. A treatise on such an important subject has long been overdue The advent of this book which deals with previous aspects of diffusion through solids will certainly be welcome to those who are interested in the subject. The subject has been dealt quite exhaustively and systematically, and a balance between the theory, experimental methods and their interpretations have been maintained. The lists of permeability and diffusion constants given in this book are really valuable. The get up of the book is nice when we consider the difficulties associated with the incidence of war. We expect that the book will prove useful and will have wide circulation which it fully merits.

S. N. M.

ON THE COMPOSITION AND CONSTITUTION OF ETHYLENEBIGUANIDE

By Kshitisranjan Chakravarty and Priyadaranjan Rây

While preparing ethylenebiguanide according to the method proposed by Dittler, and followed by Dübsky and co-workers, it was found that the product, obtained by us, differed from that of Dittler as revealed by its properties and composition. The analysis of the product showed that it was a dibiguanide and should be named ethylene-dibiguanide. This is further verified by the analysis of its copper derivatives.

In course of an investigation on metal-biguanide complexes, ethylenebiguanide sulphate was prepared in accordance with the method described by Dittler (*Monatsh*, 1908, **29**, 647). The substance, on analysis, was found to differ in composition from that of Dittler and to possess somewhat different properties. Dübsky, Langer and Strand (*Collection*, 1938, **10**, 111), who prepared the same substance following Dittler's method, assumed the composition given by the latter worker without making a complete analysis of the product. The results of analysis by different workers of their products are given below.

	Dittler (dried at 105°)	Dübsky and co-workers (dried at room temperature)	Chakravarty and Rây (thrice recrystallised and dried at room temp.)
C	21·54%	...	16·10, 15·85%
H	.. 4·76	...	4·70, 5·31
N	... 31·25	33·76	30·40, 31·0
SO_4	... 42·67	43·41	42·50, 42·50
			H_2O (by loss at 105°) ... 5·90%
			(SO_4 for the anhydrous substance) ... 45·15, 45·20%

Calc. for $(C_4H_9N_5)$, H_2SO_4 : C, 21·33; H, 4·89; N, 31·11; SO_4, 42·73 %.
Calc. for $(C_6H_{16}N_{10})\cdot 2H_2SO_4.1\cdot 5H_2O$: C, 15·96; H, 4·20; N, 31·04; SO_4, 42·57 (when anhydrous, 45·29); H_2O, 6·0%.

The method of preparation described by Dittler is given below.

One mol. of ethylenediamine hydrochloride (8 g.) and one mol. of dicyandiamide (5g.) in a finely divided condition were melted together with continuous stirring to a homogeneous viscous mass at a temperature of 140-50°. The process was stopped at the latter temperature, since decomposition set in at a few degrees higher. From the aqueous solution of the melt, the unused dicyandiamide was removed by repeated crystallisation. The filtrate, after some evaporation, was treated with a solution of copper sulphate. An immediate voluminous rose-red silky precipitate was obtained. For purification the precipitate was dissolved in dilute sulphuric acid till the red colour disappeared and reprecipitated with caustic soda. The product was washed with cold water. {Yield : 7 g. from 26 g. of the mixture (approx. 25%)}.

The copper ethylenebiguanide compound was found by Dittler to be somewhat soluble in cold water and easily soluble in caustic liquor with a red colour (in viel kaltem Wasser etwas, in Natronlauge leicht mit roter Farbe gelöst werden könnte.). He recrystallised the copper compound from hot water for analysis.

For the preparation of ethylenebiguanide sulphate the above-described copper compound was dissolved in the least possible quantity of very dilute sulphuric acid ; copper was removed by H_2S. The filtrate, on treatment with alcohol, gave a needle shaped crystalline precipitate, which was washed with alcohol. This was pure ethylenebiguanide sulphate, having the composition, $(C_4H_9N_5)\cdot H_2SO_4$.

Dübsky and co-workers, who followed the same method, obtained, however, a very poor yield of the copper compound : only 3 g. from 50 g. of the mixture (50 g. melange reactionnel ne donnent que 3 gr. de produit cuivrique).

The maximum yield obtained by us following this method, never exceeded 0·5g. of the copper compound from 13g. of the mixture containing the starting substances. We, however, succeeded in considerably improving the yield by the previous addition of a small quantity of copper sulphate (1 g.) to the reaction mixture (13 g.) and maintaining it with constant stirring at 140-45° for a sufficiently long time (1 hour) in order to obtain a perfectly homogeneous blue-coloured mass. On treatment with slightly ammoniacal water, the copper compound was left behind as rose-red, insoluble, silky residue. (Yield, 1·5 g. from 13 g. of the mixture). Further improvement in the yield was made by using mixtures in the proportion of 1 mol. ethylenediamine hydrochloride and 2 mol. of dicyandiamide. Mr. H. Sahu in this laboratory obtained an yield of about 9·5 g. of the copper compound by fusing a mixture of 20 g. ethylenediamine hydrochloride, 25 g. dicyandiamide and 8 g. copper sulphate. The copper compound as prepared by us, and presumably that of Dübsky and co-workers, was, unlike that of Dittler's product, very sparingly soluble in cold water, and we failed to recrystallise the product as Dittler had done.

For the preparation of ethylenebiguanide sulphate from its copper derivative we made a departure from Dittler's procedure. The copper compound was decomposed with moderately strong (1:1) sulphuric acid in the cold. On cooling the mixture, practically the whole of the ethylenebiguanide sulphate separated out in large rectangular prismatic crystals. These were recrystallised from a large quantity of hot water, containing a little sulphuric acid. Thus prepared, the substance was found to be difficultly soluble in cold water and perfectly stable in air: whereas Dittler describes his ethylenebiguanide sulphate as a hygroscopic, though not deliquescent, salt easily soluble in water, but insoluble in alcohol and ether. "Das Salz ist hygroskopisch, aber nicht zerfliesslich, in Wasser leicht, in Alkohol und Aether nicht löslich."

Dittler's product therefore differs from ours and possibly also from that of Dübsky and co-workers, in its solubility and capacity for hydration, besides in composition already referred to.

The composition of the copper compound also differs in a similar manner. The following table gives the results of analysis of the copper derivative as found by different workers.

Dittler.	Dübsky & co-workers.	Chakravarty & Rây.
Cu : 13·44, 13·47 %	14·74,%	14·73, 14·71 %
Do (anhydrous): 15·06, 15·10	...	16·43, 16·32
SO_4: 20·10, 20·40	22·70	22·32
Do (anhydrous) : 23·23, 23·58	...	24·77
N: ...	33·57	32·40
C: ...	...	17·10
H: ...	...	4·96
H_2O(by loss at 110°): 11·90, 11·31 %	6·36%	12·20%

Calc. for $(C_4H_8N_5)_2.Cu.H_2SO_4.3H_2O$...(Dittler) :—

Cu, 13·60; SO_4, 20·53 ; N, 30·0 ; C, 20·53 ; H, 5·13 ; H_2O, 11·55%.

Calc. for $(C_4H_8N_5)_2.Cu.H_2SO_4.H_2O$...(Dübsky & co-workers) :—

Cu, 14.73 ; SO_4, 22·24 ; N, 32·44 ; C, 22·24 ; H, 4·63 ; H_2O, 4·17%.

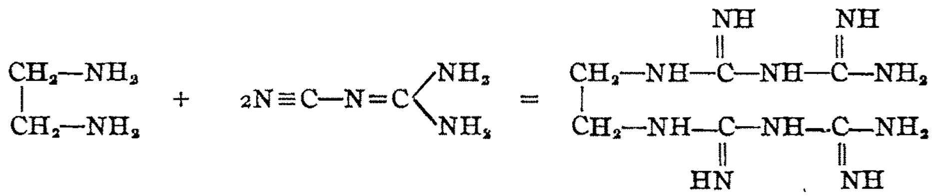
Calc. for $(C_6H_{14}N_{10})$. $Cu.H_2SO_4.2·5H_2O$...(Chakravarty and Rây) :—

Cu, 14·70 ; SO_4, 22·19 ; N, 32·36 ; C, 16·64 ; H, 4·85 ; H_2O, 10·40%,

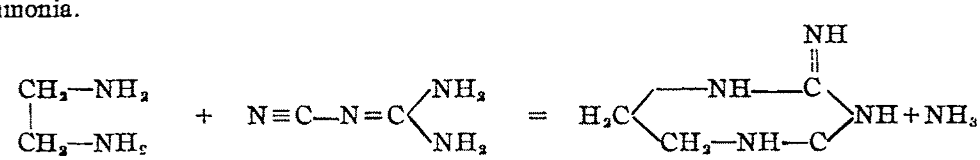
The anhydrous $(C_6H_{14}N_{10})$. $Cu.H_2SO_4$ requires Cu, 16·41 ; SO_4, 24·77%.

An analysis of the corresponding complex copper chloride, also prepared by us, gave the following results : Cu, 16·46 ; Cl, 18·30 ; N,36·10 ; C, 18·20, 18·76 ; H, 5·20, 5·31%. $(C_6H_{14}N_{10})$. Cu.2HCl. 1·5H_2O requires Cu, 16·32 ; Cl, 18·22 ; N, 35·93 ; C, 18·48 ; N, 4·88 per cent.

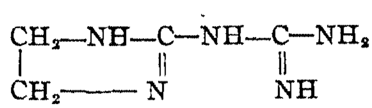
From a consideration of all the facts it may be concluded that the product, as obtained by us, differs from that of Dittler in composition. Regarding its constitution it may be represented as ethylene-dibiguanide as shown below ; and its mechanism of formation therefore follows that of simple biguanide :



Dittler represents the formation of his product, the ethylene monobiguanide, as follows, in which 1 mol. of ethylenediamine reacts with 1 mol. of dicyandiamide with liberation of 1 mol. of ammonia.



As ethylene monobiguanide, according to Dittler, forms a seven membered ring, which would lead to its instability, Dübsky and co-workers suggested a different constitution for this compound with a five-membered ring :



But we have failed to obtain ethylene monobiguanide even by closely following Dittler's method.

It is therefore concluded that the product, obtained by us, is ethylene-dibiguanide ; and its formation proceeds in the same way as that of *meta*phenylenedibiguanide (*cf.* Cohn, *J. prakt. Chem.*, 1911, **84**, 394 ; Rây and Shidhanta, *J. Indian Chem. Soc.*, 1943, **20**, 200). It should therefore behave as a quadridentate molecule.

A large number of complex salts of ethylene-dibiguanide with metals like copper, nickel and cobalt have been described in a previous paper (Rây and Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 291).

Our best thanks are due to Mr. N. N. Ghosh, M.Sc. for the estimation of carbon and hydrogen of the compounds described here.

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SYNTHESIS OF COUMARINS FROM o-HYDROXY-ARYL ALKYL KETONES. PART V. FORMATION OF COUMARINS FROM o-HYDROXYPHENYLBENZYL KETONES

By Duhkhaharan Chakravarti and Bankim Chandra Bera

5-Methyl-, 5-chloro-., 3-chloro-5-methyl-2-methoxyphenylbenzyl ketones have been condensed with ethyl bromoacetate and ethyl α-bromopropionate under Reformatsky's condition to give hydroxy-esters which on dehydration and demethylation yield coumarin derivatives in quantitative yields

The *o*-hydroxy-aryl alkyl ketones have been conveniently used by Chakravarti *et al* (Chakravarti and Mazumdar, *J. Indian Chem. Soc.*, 1938, **15**, 136; Chakravarti and Datta, *ibid.*, 1940, **17**, 65) for the synthesis of coumarin derivatives. The present investigation has been undertaken to study the applicability of this synthetical method starting with *o*-hydroxyphenyl benzyl ketones.

The ketones *e.g.*, 5-methyl-2-methoxy-, 5-chloro-2-methoxy- and 3-chloro-5-methyl-2-methoxyphenyl benzyl ketones have been condensed with ethyl bromoacetate and with ethyl α-bromopropionate forming hydroxy-esters, which have been treated with thionyl chloride and pyridine to yield unsaturated esters. These unsaturated esters on being treated with hydriodic acid yield coumarins quantitatively.

Ketones used.	Halogenated fatty esters.	Coumarins obtained
5-Methyl-2-methoxyphenyl benzyl ketone	Ethyl bromoacetate	4-Benzyl-6-methylcoumarin
Do	Ethyl α-bromopropionate	3:6-Dimethyl-4-benzylcoumarin
5-Chloro-2-methoxyphenyl benzyl ketone	Ethyl bromoacetate	4-Benzyl-6-chlorocoumarin
Do	Ethyl α-bromopropionate	3-Methyl-4-benzyl-6-chlorocoumarin
3-Chloro-5-methyl-2-methoxyphenyl benzyl ketone	Ethyl bromoacetate	4-Benzyl-6-methyl-8-chlorocoumarin
Do	Ethyl α-bromopropionate	3:6-Dimethyl-4-benzyl-8-chloro-coumarin

Experimental

Preparation of 4-Benzyl-6-methylcoumarin and 3:6-Dimethyl-4-benzylcoumarin from 5-Methyl-2-hydroxyphenyl benzyl Ketone.

5-Methyl-2-hydroxyphenyl benzyl ketone was prepared from the phenylacetate of *p*-cresol (20 g.) and anhydrous aluminium chloride (20 g.). The mixture was heated to 130-35° in absence of moisture for about ½ hour. The glassy mass was decomposed with ice-cold hydrochloric acid and it was extracted with ether, the ethereal solution was washed with sodium carbonate solution and water. It was then dried over anhydrous sodium sulphate, the ether distilled off and the product distilled at 195-99°/6 mm. as a colourless oily liquid which on standing solidified to colourless crystals, m.p. 63°, yield 16 g. It is identical with the compound prepared by Auwers (*Ber.*, 1920, **53**, 2277) from *p*-cresol methyl ether and phenylacetyl chloride.

5-Methyl-2-methoxyphenyl benzyl ketone was obtained by the methylation of the above ketone with methyl iodide in alcoh lic sodium ethoxide solution. It distilled at 193°/2 mm. as a colourless thick oil. The methyl ether has been described by Auwers (*loc. cit.*) to boil at 205-207° /14 mm.

Ethyl 5-Methyl-2-methoxy-β-benzyl Cinnamate.—A mixture of 5-methyl-2-methoxyphenyl benzyl ketone (7 g.), freshly distilled ethyl bromoacetate (10 g.), zinc wool (5 g.) and dry benzene (50 c.c.) was heated on a boilling water-bath for about 2 hours, when the zinc dissolved. After cooling the solution was poured into ice-cold dilute sulphuric acid solution. The benzene layer was separated, washed wlth dilute sodium carbonate and then with water and dried over anhydrous sodium sulphate. On removing benzene the hydroxy-ester was distilled at 215-20°/3 mm. as a light brown oil. The hydroxy-ester was converted into the unsaturated ester with thionyl chloride in presence of dry pyridine in dry ice-cold ethereal solution in the usual manner. It was distilled at 200-205°/3 mm. as a thick brown oil, which solidified on keeping for a few days. (Found: C, 77·64; H, 6·86. $C_{20}H_{22}O_3$ requires C, 77·42; H, 7·09 per cent).

4-Benzyl-6-methylcoumarin was obtained by demethylation of the above unsaturated ester with hydriodic acid (sp. gr. 1.7) for 2 hours. It was crystallised from dilute alcohol as brilliant colourless crystals, m.p. 148°. (Found: C, 81·24; H, 5·60. $C_{17}H_{14}O_2$ requires C, 81·60; H, 5·60 per cent). The same coumarin was smoothly obtained from the ethoxy derivative of 5-methyl-2-hydroxyphenyl benzyl ketone.

5-Methyl-2-ethoxyphenyl benzyl ketone was prepared in the usual way from 5-methyl-2-hydroxyphenyl benzyl ketone by heating with ethyl iodide in presence of alcoholic sodium ethoxide solution. It distilled at 200-201°/5 mm. as a yellow oil. (Found: C, 80·04; H, 7·35. $C_{17}H_{18}O_2$ requires C, 80·32; H, 7·09 per cent). *Ethyl 2-ethoxy-5-methyl-β-benzyl cinnamate* was obtained by dehydration with thionyl chloride and pyridine of the unsaturated ester, prepared by the condensation of 5-methyl-2-ethoxyphenyl benzyl ketone and ethyl bromoacetate in the presence of zinc wool. It distilled at 210-15°/ 5 mm. as a deep brown oil. (Found: C, 77·40; H, 7·22. $C_{21}H_{24}O_3$ requires C, 77·78; H, 7·41 per cent). *4-Benzyl-6-methylcoumarin* was obtained from the above unsaturated ester by heating with hydriodic acid as usual, m.p. 148° (mixed m.p. with the compound prepared above).

3:6-Dimethyl-4-benzylcoumarin.—*Ethyl 2-methoxy-α: 5-dimethyl-α-β-benzyl cinnamate* was obtained by the dehydration with thionyl chloride and pyridine of the unsaturated ester, prepared by the condensation of 2-methoxy-5 methyl benzyl ketone with ethyl α-bromopropionate in the presence of zinc wool. It distilled at 203°/2·5 mm. as a thick brown viscous liquid, which did not solidify on cooling. (Found: C, 77·76; H, 7·47. $C_{21}H_{24}O_3$ requires C, 77·78; H, 7·41 per cent). Demethylation of the above unsaturated ester gave *3:6-dimethyl-4-benzylcoumarin*, which crystallised from dilute alcohol as colourless shining needles, m.p. 136°. (Found: C, 81·74; H, 6·04. $C_{18}H_{16}O_2$ requires C, 81·82; H, 6·06 per cent).

Preparation of 4-*Benzyl-6-chlorocoumarin and* 3-*Methyl-4-benzyl-6-chlorocoumarin from* 2-*Hydroxy-5-chlorophenyl benzyl Ketone.*

2-Methoxy-5-chlorophenyl benzyl ketone was obtained by the methylation with methyl iodide in alcoholic sodium ethoxide solution of 2-hydroxy-5-chlorophenyl benzyl ketone, prepared from 4-chlorophenyl methyl ether and phenylacetyl chloride according to the method of Wittig (*Annalen*, 1925, **446**, 169). Attempts to prepare 2-hydroxy-5-chlorophenylbenzyl ketone from the phenyl acetate of *p*-chlorophenol by Fries' rearrangement were unsuccessful.

4-*Benzyl-6-chlorocoumarin.—Ethyl 2-methoxy-5-chloro-β-benzylcinnamate*, prepared by the reaction of 2-methoxy-5-chlorophenyl benzyl ketone and ethyl bromoacetate and the subsequent dehydration of the unsaturated ester with thionyl chloride and pyridine in the usual manner, distilled at 208°/4 mm. as a pale brown thick oil. (Found: Cl, 11·13. $C_{19}H_{19}O_3$ Cl requires Cl, 10·74 per cent). The unsaturated ester on heating with hydriodic acid gave 4-*benzyl-6-chlorocoumarin*. It crystallised from rectified spirit as colourless crystals, m.p. 101°. (Found: Cl, 12·99. $C_{16}H_{11}O_2Cl$ requires Cl, 13·12 per cent).

3-*Methyl-4-benzyl-6-chlorocoumarin.—Ethyl 2-methoxy-5-chloro-α-methyl-β-benzyl cinnamate* was prepared by the condensation of 2 methoxy-5-chlorophenyl benzyl ketone and ethyl α-bromopropionate in the presence of zinc wool and subsequent dehydration of the hydroxy-ester with thionyl chloride and pyridine in the usual manner. It distilled at 212°/2 mm. as a yellow oil. (Found: Cl, 10·32. $C_{20}H_{21}O_3$ Cl requires Cl, 10·30 per cent). The unsaturated ester on demethylation with hydriodic acid gave 3-*methyl-4-benzyl-6-chlorocoumarin*, which crystallised from rectified spirit as colourless needles, m.p. 162°. (Found: Cl, 12·43. $C_{17}H_{13}O_2$ Cl requires Cl, 12·48 per cent).

Preparation of 4-Benzyl-6-methyl-8-chlorocoumarin and 3:6-Dimethyl-4-benzyl-8-chlorocoumarin from 2-Hydroxy-3-chloro-5-methylphenyl benzyl Ketone.

3-*Chloro-5-methyl-2-hydroxyphenyl benzyl ketone* was prepared by means of Fries' reaction on 2-chloro-4-methylphenyl acetate (pale yellow oil, b.p. 201°/6·5 mm.) obtained by condensing 2-chloro-4-methylphenol (Mazzara and Lumbuti, *Gazzetta*, 1896, **26**, 399) with equimolecular proportion of phenylacetyl chloride. It was obtained as light yellow needles, m.p. 110°. (Found: C, 68·68; H, 4·80. $C_{15}H_{13}O_2Cl$ requires C, 69·09; H, 4·99 per cent).

3-*Chloro-5-methyl-2-methoxyphenyl benzyl ketone*, prepared as usual from 3-chloro-5-methyl-2-hydroxyphenyl benzyl ketone with methyl iodide in presence of alcoholic sodium ethoxide solution, distilled at 195-200°/ 3·5 mm. as a light yellow oil. (Found: Cl, 12·96. $C_{16}H_{15}O_2Cl$ requires Cl, 12·93 per cent).

4-*Benzyl-6-methyl-8-chlorocoumarin.—Ethyl 2-methoxy-3-chloro-5-methyl-β-benzyl cinnamate* was obtained by the condensation of 2-methoxy-3-chloro-5-methylphenyl benzyl ketone and ethyl bromoacetate in the presence of zinc wool and subsequent dehydration of the hydroxy-ester with thionyl chloride and pyridine. It distilled at 210-15°/4·5 mm. as a very thick brown oil. (Found: Cl, 10.16. $C_{20}H_{21}O_3Cl$ requires Cl, 10·30 per cent). 4-*Benzyl 6-methyl-8-chlorocoumarin* was obtained by the demethylation of this unsaturated ester with hydriodic acid. It crystallised from rectified spirit as colourless shining needles, m.p. 161°. (Found: Cl, 12·50. $C_{17}H_{13}O_2$ Cl requires Cl, 12·48 per cent).

3:6-*Dimethyl-4-benzyl-8-chlorocoumarin.—Ethyl 2-methoxy-3-chloro-α:5-dimethyl-β-benzyl cinnamate* was prepared by the condensation of 2-methoxy-3-chloro-5-methylphenyl benzyl ketone and ethyl α-bromo-propionate in the presence of zinc wool and the subsequent dehydration of the hydroxy-ester with thionyl chloride as usual. It distilled at 210°/2 mm. as a pale yellow liquid. (Found: Cl, 9·76. $C_{21}H_{23}O_3$ Cl requires Cl, 9·90 per cent). The unsaturated ester on demethylation with hydriodic acid gave 3:6-*dimethyl-4-benzyl-8-chlorocoumarin*, which crystallised from dilute alcohol as colourless shining needles, m.p. 173°. (Found: Cl, 11·89. $C_{18}H_{15}O_2$ Cl requires Cl, 11·89 per cent).

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COMPLEX COMPOUNDS OF BIGUANIDE WITH TERVALENT METALS. PART XI. SILVER (Ag^{III}) ETHYLENE-DIBIGUANIDE HYDROXIDE AND ITS SALTS

By Priyadaranjan Rây and Kshitishranjan Chakravarty

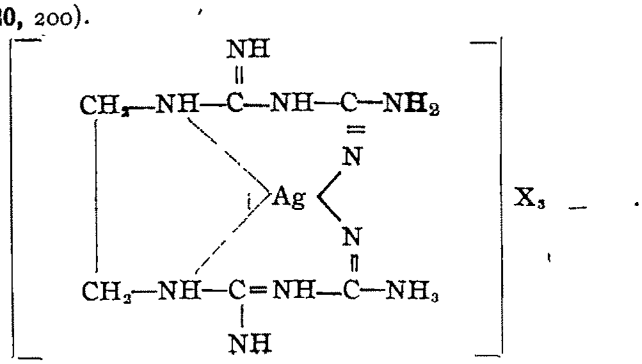
A complex silver ethylene-dibiguanide hydroxide and its salts, in which the quadri-covalent central silver atom shows, rather strikingly, a primary valency of three, have been prepared. Their composition is given by: $[Ag^{III} En (BigH^+)_2]X_3$; where X=$SO_4$, NO_3, ClO_4 or OH; and En(BigH)$_2$ = one molecule of ethylene-dibiguanide, $C_6N_{10}H_{16}$, which behaves as a quadridentate molecule. The salts form beautiful, needle-shaped, prismatic crystals of deep red colour, the base being violet-red. These are quite stable at ordinary temperatures, and the nitrate can be recrystallised from warm dilute nitric acid.

The compounds liberate *two* equivalents of iodine for every atom of silver from acidified KI solution. The molecular conductivity of the nitrate corresponds to that of a tervalent complex ion. Unlike that of bivalent silver the new complex is *diamagnetic*.

A tervalent silver atom should possess an electronic configuration similar to that of bivalent nickel and palladium, and hence its complexes would be diamagnetic like those of nickel and palladium if the co-ordination bonds be of the planar, hybrid d-s-p^2 type. Tervalent silver thus resembles tervalent gold of the same periodic group forming quadri-covalent planar complexes of the penetration class.

In a previous paper published from this laboratory (Rây and Ghosh, *J. Indian Chem. Soc.*, 1943, **20**, 291) complex salts of ethylene-dibiguanide with bivalent metals like copper, nickel and cobalt have been described. An attempt to prepare similar complexes with bivalent silver led, however, to an unexpected result. When ethylene-dibiguanide sulphate was made to react with silver salt solution in presence of potassium or sodium persulphate, a bright red, silky, crystalline substance slowly separated out as a precipitate in which the silver atom was found to behave as a tervalent element. Oxidation with persulphate usually leads to the formation of bivalent silver complexes (Barbieri, *Gazzetta*, 1912, **42**, 7; *Ber.*, 1927, **60**, 2424; Hieber and Mühlbauer, *Ber.*, 1928, **61**, 2149; Morgan and Burstall, *J. Chem. Soc.*, 1930, 2594). The co-ordinating molecules, employed in all these cases, were mostly bidentate in character, acting in slightly acid or neutral solution, except, of course, in the case of mono-dentate pyridine. The higher stage of oxidation in the present case might therefore be connected with the quadridentate nature of the associating unit, which presumably exercises a great stabilising effect on the complex structure, and also related to a possible higher oxidation potential of the persulphate as the reaction was allowed to proceed in a fairly acid medium.

The constitution of this tervalent silver complex is shown below, following that suggested for *meta*phenylene-dibiguanide complexes of copper and nickel (Rây and Siddhanta, *J. Indian Chem. Soc.*, 1943, **20**, 200).



where X=SO_4, NO_3, ClO_4 or OH.

The salts form beautiful silky crystals of red colour, the base being violet-red. They are fairly stable in the solid state at the ordinary temperature. The sulphate was more or

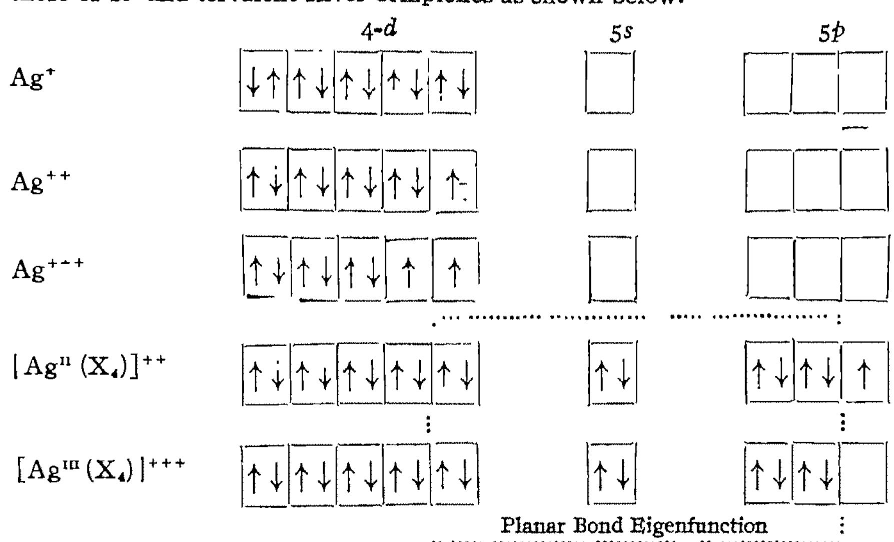
less dehydrated by heating to 80° without any appreciable decomposition. They liberate two equivalents of iodine per silver atom in the molecule from acidified KI solution. The molecular conductivity of the nitrate at 20° was found to be 518 $ohms^{-1}$ (approx.) at infinite dilution. This agrees well with values for tervalent complex ions. Unlike the complex salts of bivalent silver, which are all paramagnetic like those of bivalent copper, the complex silver (Ag^{III}) ethylene-dibiguanide salts are all diamagnetic.

The occurrence of silver in a state of oxidation, higher than what corresponds to AgO or Ag_2O_3, is not altogether unknown. Luther and Pokorny (*Z. anorg. Chem.*, 1908, **57**, 290) have shown that the peroxide of silver formed by electrolytic oxidation of a silver anode in sulphuric acid and the so-called peroxynitrate and other similar salts of silver, prepared by electrolytic oxidation of neutral solutions of silver salts, consist essentially of the peroxide Ag_2O_3 with occluded or adsorbed silver salts in the latter case. Silver therefore behaves in this case as a tervalent element, if, of course, the formation of a ring compound or a chain of oxygen atoms be excluded.

Higson (*J. Chem. Soc.*, 1921, **119**, 2048), by the action of a solution of sodium persulphate on metallic silver as well as on a solution of silver nitrate in the cold, obtained a product which consisted of a peroxide of the approximate composition, Ag_3O_4.

Recently Malatesta (*Gazzetta*, 1941, **71**, 580) has reported the preparation of acid sodium salts of a complex silver telluric acid, $Na_6H_3\,[Ag^{III}(TeO_6)_2]$ and $Na_7H_2\,[Ag^{III}(TeO_6)_2]$, in which the silver atom serves as the centre of the anionic complex. As, owing to war conditions, the original paper is not available here, we are not in a position to discuss about the nature and stability of this complex salt.

The electronic configuration of a tervalent silver atom should resemble that of bivalent nickel and palladium, just as bivalent silver is analogous to bivalent copper in its outer electronic structure. Hence a quadri-covalent complex of tervalent silver should be, as has been actually found, diamagnetic in character, if the co-ordination bonds be of the hybrid planar *d-s-p*^{2} type as in the corresponding bivalent nickel and palladium complexes. In fact, this serves as a confirmation of tervalency of silver in these complex salts. This is apparent from the electronic structures in the outermost levels of uni-, bi- and tervalent silver ions and those of bi- and tervalent silver complexes as shown below.



In silver the first three quantum levels as well as $4s$ and $4p$ levels representing the krypton core, are completely filled up with electrons and are not shown in the above scheme.

That a tervalent silver atom gives a co-ordination number of four and not six, which is characteristic of a large number of other tervalent ions, is perfectly in keeping with its position between copper and gold in the same group of the Periodic Table. A tervalent gold, as is well known, always forms a quadri-covalent complex; and Burawoy, Gibson, Hampson and Powell (*J. Chem. Soc.*, 1937, 1690) have shown by crystallographic examination that diethyl monobromogold, $(C_2H_5)_2AuBr$, gives a square planar structure by polymerisation. There is therefore nothing unusual in that the silver atom shows the character of both copper and gold, becoming uni-, bi- and tervalent respectively as well as quadri-covalent in its complexes for the latter two cases.

EXPERIMENTAL

Silver Ethylene-dibiguanidinium Sulphate.—A solution of 0·3 g. of silver sulphate in 60 c.c. of water was mixed with a solution of 1 g. of ethylene-dibiguanide sulphate in 200 c.c. water. The mixture was cooled and treated with 1 g. of potassium persulphate dissolved in a little water. This was then diluted to about 550 c.c. and kept in the cold for about 18 hours with occasional stirring. A beautiful silky crystalline precipitate of red colour gradually separated from the solution. This was filtered, washed with cold water and then dried on a porous plate. The crystals were kept over $CaCl_2$ in a desiccator in the cold.

The substance is sparingly soluble in water. In the solid state it can be heated to 80° without appreciable decomposition. A solution of the pure substance in water or dilute sulphuric acid can be heated on the water-bath without any detectable change. In concentrated sulphuric acid it dissolves to form a red solution. The salt keeps unchanged at ordinary temperature for a pretty long time. On qualitative examination the substance was found to be free from persulphate. {Found: C, 13·60; H, 4·30; N, 26·50, 26·40, 26·30; Ag, 19·86, 19·70, 19·60; SO_4, 27·0, 26·40, 26·25; H_2O (by loss at 80°), 10·40 per cent}. 0·0954 G. of the substance liberated 6·9 × 1·0166 c.c. of $N/20$ iodine; Ag as Ag^{III}, 19·83; 0·1592 g. of the substance liberated 11·475 × 1·0166 c.c. of $N/20$ iodine; Ag^{III}, 19·75; 0·1918 g. of the substance liberated 7·0 c.c. of $N/10$ iodine; Ag^{III}, 19·70 per cent. $[Ag^{III}En(BigH^+)_2](SO_4)_{1\cdot5}$, 3·5 H_2O requires C, 13·31; H, 4·44; N, 25·88; Ag, 19·96; SO_4, 26·61; H_2O, 11·65 per cent. $En(BigH)_2 = C_6N_{10}H_{16}$ = a molecule of ethylene-dibiguanide.

It gave a diamagnetic susceptibility of $\chi_g = -0{\cdot}394 \times 10^{-6}$.

The Base.—The complex sulphate was decomposed with cold 15% solution of sodium hydroxide or potassium hydroxide. The product was washed by decantation with cold alkaline water (containing a few drops of N-NaOH or KOH) till free from sulphate and then finally with cold water. It forms violet-red microcrystalline mass resembling permanganate in colour. This was dried as described above.

The base is sparingly soluble in water and reacts strongly alkaline to litmus. It decomposes on heating with water.

Found: N, 32·10, 31·95, 32·20; Ag, 24·45, 24·20, 24·40; 0·2260 g. of the substance liberated 20 × 1·0166 c.c. of $N/20$ iodine; Ag^{III}, 24·35; 0·1343 g. liberated 10·95 × 1·0166 c.c. of $N/20$ iodine; Ag^{III}, 22·45; 0·1174 g. liberated 9·35 × 1·0166 c.c. of $N/20$ iodine; Ag^{III}, 21·85%. $[Ag^{III}En(BigH^+)_2](OH)_3$, $3H_2O$ requires N, 31·75; Ag, 24·49 per cent.

The last two samples show some sign of reduction.

The mass susceptibility, $\chi_g = -0{\cdot}393 \times 10^{-6}$.

The Nitrate.—This was prepared by treating the moist base with a cold solution of N-HNO_3. The violet-red base changed into orange-red crystals of the nitrate. These were recrystallised from hot dilute nitric acid ($2N$). The crystals were washed with cold water containing a few drops of nitric acid and then dried as in the previous cases.

The nitrate is moderately soluble in water, the solution decomposes on boiling with decolourisation. It can be boiled in dilute nitric acid solution without any noticeable change.

Found: C, 13·80; H, 3·64, N (total), 35·0, 35·0, 35·0; Ag, 20·75, 20·34, 20·52 per cent. NO_3 (by nitron), 36·0; 0·1148 g. of the substance liberated $8·6 \times 1·0166$ c.c. of $N/20$ iodine; Ag^{III}, 20·55; 0·1504 g. liberated $11·25 \times 1·0166$ c.c. of $N/20$ iodine; Ag^{III}, 20·50: 0·1311 g. liberated $10·10 \times 1·0166$ c.c. of $N/20$ iodine; Ag^{III}, 20·65 per cent. $[Ag^{III} En (BigH^+)_2] (NO_3)_3$ requires C, 13·80; H, 3·07; N (total), 34·87; Ag 20·69; NO_3, 35·63 per cent.

Magnetic susceptibility, $\chi_g = -0·402 \times 10^{-6}$.

Molecular conductivity

$t = 20°$.

v (dilution in g. mol. per litre)	... 488	976	1952	3904
μ_v	... 362·5	397·0	429·8	467·8

μ_∞(by extrapolation) = 518·0 approx.

The Perchlorate.—This was prepared by treating the moist base with cold 60% perchloric acid solution, added drop by drop, till the violet-red base changed completely into the dark red shining crystals of the perchlorate. The mixture was cooled strongly in ice. The crystals were filtered on the pump and dried on a porous plate. These were kept as usual in the cold over $CaCl_2$ in a desiccator. The substance is highly soluble in water.

Found: N, 21·35; Ag, 16·70, 16·40; ClO_4, 43·40; 0·2675 g. of the substance liberated $16·20 \times 1·0166$ c.c. of $N/20$ iodine; Ag^{III}, 16·75; 0·1635 g. liberated $9·90 \times 1·0166$ c.c. of $N/20$ iodine; Ag^{III}, 16·60 per cent. $[Ag^{III} En(BigH^+)_2] (ClO_4)_3$, 1·5 H_2O requires N, 21·16; Ag, 16·31; ClO_4, 45·10 per cent.

The base, on treatment with cold NH_4HF_2 solution, gave an orange-yellow fluoride, which, however, readily lost HF when removed from the solution and turned violet-red due to more or less complete reformation of the base.

With cold $2N$-HCl the base similarly formed an orange-red chloride, which readily decomposed into white silver chloride.

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STANDARDISATION OF THE METHOD OF ESTIMATING NITRITE WITH GRIESS ILOSVAY'S REAGENT

By W. V. B. Sundara Rao

The intensity of pink colour which develops when acetic acid and α-naphthylamine act on nitrous acid is used for the estimation of nitrite in solution (Griess, *Ber.*, 1879, **12**, 427; Ilosvay, *Bull. Soc. Chim.*, 1889 *iii*, **2**, 317, 388; Richardson and Hollings, *J. Soc. Chem. Ind.*, 1903, **22**, 616). In the process sulphanilic acid is converted by the nitrous acid into the corresponding diazo compound and the latter reacts with the α-naphthylamine to form α-naphthylamine-*p*-azobenzene-*p*-sulphonic acid, a pink azo dye. In view of the difficulty of maintaining standard sodium nitrite solution for comparison of the tint with that of the sample, in a nephelometer, resort is usually taken to compare the colour with the Lovibond's glass tints. At present the reaction is allowed to take place in the cold for this purpose. In literature different concentrations of the reagents are recommended but enough time is not usually allowed for the development of maximum tint (Richardson and Hollings, *loc. cit.*; Snell "Colorimetric Method of Analysis," 1941, I, p. 644). In the above cases the tint developed in the test solution was compared with the tint of standard sodium nitrite solution and as such it was not necessary to wait till the maximum intensity was reached. It was enough if the reagents were added in the test solution as well as in standard sodium nitrite solution at the same time and the period allowed for the development of the tint was the same in both the solutions. When the tint is to be compared with the Lovibond's glass tints, it is essential that the maximum tint is developed before the comparison can be made. While determining nitrites in soils and culture solutions in connection with chemical and microbiological work, it was observed that the maximum tint was not obtained even in 2 hours, and the period taken for this purpose varied widely on different occasions. Hence an attempt was made to standardise this method.

Reagents employed by different workers differed only in the concentration of sulphanilic acid, α-naphthylamine and acetic acid (Snell, *loc. cit.*; Briggs, *J. Biol. Chem.*, 1923, **57**, 351: "Methods of Analysis, A.O.A.C.", 1940, 5th Ed., p. 527, Washington, D.C.). In A.O.A.C. hydrochloric acid instead of acetic acid is used. In this present investigation it was observed that with each of these reagents intensity of the colour increased gradually and the maximum intensity was reached in about 3 hours. The use of higher concentrations of sulphanilic acid, and α-naphthylamine did not result in the reduction of the time taken for maximum colour development. Further it was noticed that the order of addition or variation in relative amounts of the two reagents had no effect on this period.

The only factor that appeared to affect appreciably the time required for maximum colour development in a given volume of test solution containing a definite amount of nitrite, was temperature. Lunge (*Z. angew. Chem.*, 1889, **2**, 666; Lunge and Keane, "Technical Methods of Analysis,"1908; Vol. I, Part II, p. 760; Lunge *et al.*, *Z. angew. Chem.*, 1894, **7**, 348; Lunge and Keane, "Technical Methods of Chemical Analysis," 1908, Vol. I, Part I, pp. 361-376,) suggested that high intensity in colour was reached in 2 minutes at 70-80° and the delicacy of the qualitative test would be improved. So it was felt desirable to study the possibility of developing the tint in test solutions at the temperature of boiling water and comparing the tint with the Lovibond's glass tints for estimating nitrite-nitrogen. The next series

of experiments were conducted in test tubes at the temperature of boiling water in a water-bath. It was observed that with reagents (*J. Biol. Chem.*, 1923, **57**, 351) (*i*) the maximum intensity was reached within 5 minutes, (*ii*) the colour remained steady even after 3 hours, (*iii*) half the initial concentration of nitrite gave half the colour intensity showing that the colour obtained at the temperature of boiling water was proportional to the quantity of nitrite present, and (*iv*) blanks (distilled water and reagent) kept in the water-bath and treated in the same manner did not show any colour. When the colour was allowed to develop in the cold one had to wait till the maximum colour developed ; the period required for this purpose was over 3½ hours. It was not possible to fix some arbitrary interval, say ½ hour or 1 hour, since the rate of colour development was dependent on the fluctuating factor, namely, temperature. In the boiling method constant temperature was secured and the period was reduced from 3 hours to 5 minutes.

The colour intensity readings with various concentrations of standard solution of sodium nitrite prepared according to Clowes and Coleman ('Quantitative Chemical Analysis') were taken by comparing with the Lovibond's glass tints in the tintometer and the conversion factor was determined. Reading between the range of 1·5 and 4 could be relied upon, since the colour was neither too low nor too deep for comparison. By this method unknown amounts of nitrite in a test solution were correctly determined. Further the salts usually employed in culture solutions (Omeliansky's solution and nitrate broth-chlorides, nitrates, sulphates and phosphates) were found to have no interfering effect. Nitrite present in (*a*) effluent and (*b*) soil were determined by the boiling method and was compared in each case with the value got by comparison with the tint developed with standard sodium nitrite solutions. The values agreed closely showing that in the determination of nitrite-nitrogen in these substances by comparing the tint developed in the test solution with the Lovibond's glass tints, the existing cold method could with advantage be replaced by the boiling method.

As standardised the method is as follows :

The test solution is suitably diluted. An aliquot part is taken in the test tube, distilled water is added to make up to 10 c.c. and then 1 c.c. of the reagent mixture (*J. Biol. Chem.*, 1923, **57**, 351) is added. The test tube with contents is kept in the water-bath for 5 minutes at the temperature of boiling water, cooled under running tap water for 5 minutes and the reading is taken with ½″ cell by comparison with standard glass tints. The reading should be between 1·5 and 4. This is multiplied by the conversion factor previously determined to obtain the amount of nitrite-nitrogen in mg. present in the aliquot taken into the test tube. Nitrite-nitrogen is calculated later into parts per million of soil or mg. per litre of the test solution.

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PARACHOR OF POTASSIUM CHROMATE

By W. V. Bhagwat, V. A. Moghe and P. M. Toshniwal

The parachor of potassium chromate as obtained by solution method is about 195. The calculated value is 347·6. The difference is very great and cannot be explained only on the ground that atomic and ionic parachors are different.

Parachor of potassium chromate has not been determined by fusion method. Lakhani and Daroga (*J. Indian Chem. Soc.*, 1938, **15**, 40) have given the value 335·6 for the parachor of potassium chromate in aqueous solution at 35°. The calculation as shown by us (*ibid.*, 1942, **19**, 225,) are doubtful. The values as obtained by us are recorded in the following tables.

Parachor of Potassium Chromate

Parachor of water was taken to be 52·6 in all the following tables

Table I — K_2CrO_4 (3·0002 g.) dissolved in 6·5980 g. of water. $x(K_2CrO_4)$=0·04047. M_m=25·12.

Table II — K_2CrO_4 (2·0000 g.) dissolved in 6·5004 g. of water. $x(K_2CrO_4)$=0·02775. M_m=22·88.

Temp.	Density.	γ.	P_m.	P_x.	Density.	γ.	P_m.	P_x.
20°	1·294	76·86	57·51	188·0	1·209	75·67	52·82	189·6
30	1·288	76·54	57·65	190·0	1·204	74·56	55·86	190·2
40	1·283	75·58	57·73	192·5	1·200	73·03	55·79	189·09
50	1·278	74·32	57·71	192·0	1·196	72·26	55·78	189·0

Table III — K_2CrO_4 (3·5084 g.) in 6·5566 g. of water. $x(K_2CrO_4)$= 0·04858. M_m=26·55.

Table IV — K_2CrO_4 (1·0050 g.) in 6·5890 g. of water. $x(K_2CrO_4)$= 0·01398. M_m=20·46.

Table V — K_2CrO_4 (0·4978 g.) in 6·4740 g. of water. $x(K_2CrO_4)$= 0·00706. M_m=19·24.

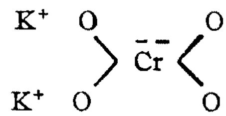
Temp.	Density	γ.	P_m.	P_x.	Density.	γ.	P_m.	P_x.	Density.	γ.	P_m.	P_x.
30°	1·328	77·13	59·24	198·9	1·107	72·57	53·96	192·3	1·055	72·02	53·09	199·9
40	1·325	77·02	59·10	190·1	1·102	70·99	53·89	188·1	1·051	70·74	53·04	197·2
50	1·321	75·34	59·14	192·4	1·098	69·92	53·89	188·0	1·047	69·10	52·96	193·4

Table VI — K_2CrO_4 (3·0932 g.) in 6·3912 g. of water. $x(K_2CrO_4)$=0·04295. M_m=25·57.

Table VII — K_2CrO_4 (2·6850 g.) in 6·8350 g. of water. $x(K_2CrO_4)$=0·03515. M_m=24·195.

Temp.	Density.	γ.	P_m.	P_x.	Density.	γ.	P_m.	P_x.
20°	1·304	79·09	58·45	202·5	1·257	79·98	57·48	205·1
30	1·300	77·71	58·42	199·5	1·254	77·98	57·33	200·8
40	1·296	76·83	58·38	198·6	1·249	76·35	57·24	198·3
50	1·290	75·34	58·37	198·3	1·242	75·43	57·41	202·6

The values as obtained for different concentrations are not very constant. The value 195 may be taken as the mean parachor of potassium chromate as observed in solution. The value is very interesting since the calculated value of parachor for potassium dichromate from atomic parachors of K, Cr, and O is 354 (K = 110, O = 20, Cr = 54). If we assume that the constitution of potassium chromate is represented as



then in addition there are two polar bonds and two semi-polar bonds each of which has a value of -1.6. Hence the above configuration gives $P_{K_2CrO_4} = 347.6$. The experimental value is nearly half of this calculated value. Taking the value of Lakhani and Daroga (*loc. cit.*) and substituting $P_{H_2O} = 52.3$ instead of 54 and applying the usual formulae the experimental value of $P_{K_2CrO_4}$ comes out to be only 225. The value of 2K alone is 220. This high discrepancy is very difficult to explain; clearly the atomic and ionic parachor cannot be identified but that alone is not enough to explain the observed low results. Further work is in progress.

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THE ACTION OF HYDROGEN SULPHIDE ON PERMANGANATES. PART II. POTASSIUM, AMMONIUM, AND BARIUM PERMANGANATES

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The action of hydrogen sulphide on permanganates of potassium, ammonium and barium has been studied. The chief products in solution are thiosulphate, dithionate and sulphate. The precipitate contains compounds having the composition, $RO \cdot nMnO_2$.

In a previous communication (Mohammad and Ahluwalia, *J. Indian Chem. Soc.*, 1941, **18**, 309) it was shown that compounds of varying composition, *i.e.*, xRO, yMnO, $z$$MnO_2$, $n$$H_2O$ were formed when hydrogen sulphide water was added to solutions of calcium and silver permanganates. It has been possible now to get some conclusive results by studying the action of hydrogen sulphide on permanganates of potassium, ammonium and barium.

Products of Reaction when Hydrogen Sulphide water is added until the purple colour of Potassium Permanganate (1%, 50 c.c.) *just disappears*

This stage of the reaction is called the *decolourisation* or the *neutral* stage. The solution after filtering off the dark brown precipitate, produced in the reaction, is neutral. On analysis it is found that 65% of total potassium (estimated by the cobaltinitrite method) are present in the filtrate. It is obvious that the rest of potassium is present in the precipitate in the combined state. The potassium in the filtrate is accounted for as thiosulphate, dithionate and sulphate (for methods of analysis, *cf.* Mohammad and Ahluwalia, *loc. cit.*). The formation of thiosulphate can be obviated if hydrogen sulphide water is added exactly up to the decolorisation stage. As the end-point is not sharp, the solution so obtained is found to be turbid and contains colloidal sulphur and oxides of manganese. Thiosulphate is also found to be absent if hydrogen sulphide is bubbled carefully up to the decolorisation stage. After the decolorisation stage, further addition of hydrogen sulphide makes the solution alkaline. Excess of hydrogen sulphide produces polysulphides of potassium in the solution and converts the dark brown precipitate into manganous sulphide.

Similar results are obtained when H_2S aq. is added to solutions of ammonium and barium permanganates. Sulphate is present as barium sulphate in the precipitate obtained by adding H_2S aq. to barium permanganate solution.

Analysis of the Precipitate

The precipitate obtained in the decolorisation stage is treated with strong hydrochloric acid and the chlorine evolved is absorbed in a concentrated solution of potassium iodide. This gives the available oxygen. The residual liquid is neutralised with solid sodium carbonate and aliquot portions from this are used for estimating potassium and total manganese (pyrophosphate method). The results, which are embodied in Table I (Expts. 1 & 2), show that the value for the molecular ratio of $K_2O : MnO_2$ is 1 : 2 and the value for the molecular ratio of $K_2O:MnO:MnO_2$ is 1:3·5:2·2. The analytical data obtained by using a current of hydrogen sulphide, also gives the same value of 1:2 for the molecular ratio of K_2O : MnO_2. However, the value of the molecular ratio for K_2O : MnO : MnO_2 becomes 1 : 4·8 : 2·1 (Table I, Expts. 3 & 4).

Morawsky and Stingle (*J. prakt. Chem.*, 1878, **18**, 2) obtained $K_2O.8MnO_2.3H_2O$ by reducing a neutral solution of potassium permanganate by alcohol, glycerol, potassium thiocyanate or potassium oxalate. Several compounds of potassium and of many other metals of similar composition have been prepared by different methods (Mellor, "Treatise on Inorganic Chemistry", Vol XII, p. 274). These compounds are regarded as the derivatives of hydrated manganese dioxide. Gorger (*Ann. chim. phys.*, 1862, *iii*, **66**, 161) and W. Biltz (*Gott. Nachr.*, 1930, 189) regard hydrated manganese dioxide as manganous acid, H_2MnO_3, so that manganese dioxide becomes manganous anhydride, MnO_2, and the salts RO, $nMnO_2$, permanganites. Wright and Manke (*J. Chem. Soc.*, 1888, **53**, 34) observed that the product obtained by reducing potassium permanganate with glycerol does not have the composition $K_2O.8MnO_2$, $3H_2O$, assigned to it by Morawsky and Stingle (*loc. cit*), for neglecting the water of crystallisation, it varied considerably in composition, *e.g.*, $K_2O.3MnO\ 6MnO_2$; $2K_2O.13MnO.22MnO_2$; and $3K_2O.\ 2MnO.\ 18MnO_2$. It was also found by them that the product of reduction of permanganate by sulphur dioxide in the cold approximated to $K_2O.2MnO.12MnO_2$. In view of the above reports the product obtained by the action of hydrogen sulphide on potassium permanganate may have the composition $K_2O.2MnO_2$, $2K_2O.7MnO.4MnO_2$ or $K_2O.5MnO.2MnO_2$ (calculated from the values given in Table I). The first composition given to the compound seems probable since in the two different sets of experiments the value of the molecular ratio of $K_2O : MnO_2$ remains constant.

TABLE I

Composition of the precipitate when the colour of $KMnO_4$ (1%, 50 c.c. *containing* 0·1238 g. *of* K) *just disappears by* H_2S

No.	H_2S aq.	K_2O.	MnO.	MnO_2.	Mol. ratio. K_2O:MnO:MnO_2.	Mol. ratio (approx.) K_2O:MnO_2
1	23 c.c	0·0519 g.	0·1376 g.	0·1078 g.	1:3·5:2·2	1 : 2
2	23 c.c	0·0518	0·1376	0·1078	1·3·5:2·2	1 : 2
3	Gas bubbled	0·04340	0·1554	0·0848	1:4·8:2·1	1 : 2
4	Gas bubbled	0·04300	0·1558	0·0843	1·4·8:2·1	1 : 2

TABLE II

Analysis of the precipitate obtained by adding increasing amounts of H_2S aq. to 50 c.c. *of* $KMnO_4$ *solution* (1%)

No.	H_2S aq.	$KMnO_4$ decomposed.	% Decomposition.	K_2O.	MnO.	MnO_2.	K_2O:MnO:MnO_2.	K_2O·MnO_2 (approx).
1	11 c.c	0·1273 g.	25·46	0·02082 g.	0·02669 g.	0·03741 g.	1:1·7 : 1·94	1:2
2	16·5	0·2313	46·26	0·02554	0·06705	0·04524	1·3·48: 1·92	1:2
3	22·0	0·2676	53·52	0·03024	0·07663	0·0535	1:3·3 : 1·9	1:2
4	27 5	0·3244	64·88	0·0407	0 08624	0·07308	1:2·8 : 1·94	1:2
5	33·0	0·3921	78·42	0·04565	0·09965	0·09396	1:2·9 : 2·2	1:2
6	38·5	0·4471	89 42	0·04663	0·1214	0·0974	1:3·4 : 2·26	1:2
7	44·0	0·5000	100 *	0·0519	0·1376	0·1078	1·3·5 : 2·2	1:2
8	50·0		—	0·0337	0·1956	0·0348	1:7·7 : 1·14	

* 100% Decomposition indicates the stage at which the purple colour of the permanganate just disappears.

In order to elucidate further the composition of the dark brown precipitate in the neutral stage, the composition of the precipitates formed in the preliminary stages of the reaction was also determined.

To solutions of potassium permanganate (50 c.c., 1%) increasing amounts of H_2S aq. were added. The precipitate obtained in each experiment was thoroughly washed and then analysed. The results of entirely separate experiments are recorded in Table II. They show:

(*i*) The changes in the manganese dioxide content correspond exactly with those of potassium and show a maximum at the decolorisation stage like that of potassium.

(*ii*) Though no constant relation is observed in the values obtained for the molecular ratios of $K_2O : MnO$, or $MnO : MnO_2$, or $K_2O : MnO : MnO_2$, yet the value of the molecular ratio of $K_2O : MnO_2$ remains constant *i.e.* 1 : 2 in all different sets of experiments. This remarkable constancy in the value for the molecular ratio of $K_2O : MnO_2$ in all the experiments and similarity in the changes of their contents in the precipitates point out the formation of the compund $K_2O.2MnO_2$. The results show that this compound is continuously formed throughout the preliminary stages of the reaction.

(*iii*) The amount of manganous oxide, calculated from the difference of total manganese corresponding to manganese dioxide, increases progressively with the addition of increasing amounts of hydrogen sulphide water. After the decolorisation stage, any excess of hydrogen sulphide reduces the manganese dioxide content in the precipitate though increase in the amount of manganous oxide is still noticed (Table II, Expt. 8). Considering the primary reduction of manganese dioxide (in the compound $K_2O.2MnO_2$) to be taking place according to the equation $MnO_2 = MnO + O$, if the amount of manganous oxide be calculated from the amount of manganese dioxide decomposed, it corresponds nearly with the observed amount of manganous oxide (Expts. 7 & 8, Table II. Decrease in the amount of MnO_2 = 0·073 g. Amount of MnO observed = 0·058 g; calculated amount of MnO = 0·059 g.). This shows that the reaction follows a definite course. Manganous oxide may be considered as the primary reduction product of manganese dioxide.

The concentration of the oxidising agent does not seem to have any effect on the composition of the precipitate, since 0·5% potassium permanganate solution, also yields similar results.

The above results are in agreement with those obtained by adding increasing amounts of hydrogen sulphide water to 1% solution of barium permanganate. The results are recorded in Table III. They show that the value of the molecular ratio for $BaO : MnO_2$ remains constant and is 1 : 2 as observed in the case of potassium permanganate.

TABLE III

Analysis of the precipitates when increasing amounts of H_2S aq. *are added to* 50 c.c. of $Ba(MnO_4)_2$ *soln.* (1%)

No.	H_2S aq.	$Ba(MnO_4)_2$ decomposed.	% Decomposition.	BaO.	MnO.	MnO_2.	Molecular ratio BaO : MnO : MnO_2.	Molecular ratio (approx.) BaO : MnO_2.
1	11 c.c.	0·1844 g.	36·88	0·0113 g.	0·0597 g.	0·01217 g.	1 : 11·4 : 1·9	1 : 2
2	14	0·2291	45·82	0·01248	0·0760	0·01304	1 : 13·1 : 1·8	1 : 3
3	17	0·3143	62·86	0·01553	0·1011	0·01956	1 : 13·9 : 2·2	1 : 2
4	20	0·3366	67·32	0·0188	0·1105	0·0204	1 : 12·6 : 1·9	1 : 2
5	23	0·4256	85·12	0·0217	0·1437	0·02108	1 : 11·8 : 1·8	1 : 2
6	26	0·4943	98·86	0·0235	0·1700	0·02108	1 : 15·6 : 1·7	1 : 2
7	32	(*i*) 0·5000	100*	0·02366	0·1697	0·0239	1 : 15·5 : 1·8	
		(*ii*) 0·5000	100	0·02300	0·1687	0·02522	1 : 16 : 1·93	1 : 2
8	37	...	...	0·01936	0·1724	0·00478	2·3 : 44·2 : 1	
9	44	...	...	0·01574	0·1864	0·00348	4 : 105 : 1	Alkaline solution.

* 100% Decomposition represents the stage at which the permanganate colour just disappears.

In order to confirm the composition of the intermediate compounds in the neutral stage, the action of hydrogen sulphide on the compounds to which similar compositions have been assigned, was studied.

The Action of Hydrogen Sulphide on Potassium Octapermanganite ($K_2O\ 8MnO_2$) *and Barium Dipermanganite* ($BaO.2MnO_2$).

Potassium octapermanganite is prepared as a dark brown precipitate by adding 2·5 c.c. of 10% solution of glycerol to 50 c.c. of 1% potassium permanganate solution. This reaction has an induction period of about half an hour which can be shortened by adding increasing volumes of 10% glycerol. The analysis of the precipitate (Table IV) shows that the compound formed has the composition, $K_2O.8MnO_2$.

TABLE IV

Analysis of the precipitate when 2·5 c.c. of 10% glycerol are added to 50 c.c. of 1% $KMnO_4$ *soln.*

No.	K_2O (g.)	MnO_2 (g.)	Molecular Ratio $K_2O:MnO_2$
1	0·0369	0·2738	1:8·04
2	0·0370	0·2734	1:8·10

TABLE V

Composition of the precipitate when the colour of NH_4MnO_4 *(0·5%, 100 c.c.) just disappears by* H_2S.

No.	H_2S aq (c.c.)	$(NH_4)_2O = 2NH_3 + H_2O$	MnO. (g.)	MnO_2 (g.)	Molecular ratio $(2NH_3 + H_2O)$: MnO : MnO_2	Molecular ratio $(2NH_3+H_2O)$. MnO_2
1	40	0·0208 g.	0·2294	0·03652	1:8·37:1·02	1 : 1
2	40	0·0202	0·2294	0·03652	1:8·39:1·05	1 : 1
3	(1% solution) 80	0·0400	0·4584	0·07348	1·8·5:1·1	1 . 1
4	80	0·0412	0·4584	0·07336	1:8·40:1·1	1 : 1

The fact that the whole of the manganese is present in the precipitate and corresponds with the total available oxygen, proves the absence of any other oxide of manganese in the precipitate. These results confirm the conclusions of Morawsky and Stingle (*loc. cit.*). It appears that Wright and Manke (*loc. cit.*) must have taken an excess of glycerol which reduces further some of the manganese dioxide into manganous oxide.

Barium dipermanganite ($BaO.2MnO_2$) is prepared by adding hydrogen peroxide to 1% solution of barium permanganate until the solution became just colourless.

When aqueous H_2S is added to potassium octapermanganite or barium dipermanganite, suspended in water, each stage, *viz.*, the neutral, the alkaline and the polysulphide observed in the reaction between hydrogen sulphide and pemanganates of potassium and barium, is noticed. Even the products and their relative amounts formed are comparable (Table VI, Expt. 4). It is interesting to note that though dithionate is formed in the neutral and the alkaline stages of the reaction, sulphate was found to be absent. The presence of sulphate can only be detected in the polysulphide stage. This is due to the decomposition of dithionate by hydrogen sulphide into thiosulphate, sulphate and sulphur (Dunnicliff and Nijhawan, *J. Chem. Soc.*, 1926, 1; Mohammad and Ahluwalia, *loc. cit.*). Similar observations are made in the reactions between hydrogen sulphide and permanganates of potassium and barium No increase in the amount of sulphate is noticeable in the alkaline stage of the reactions. Sulphate can not be detected also when H_2S aq. is mixed with precipitates obtained by the addition of H_2S into solution of potassium and barium permanganates. Since dithionate is shown to be absent in the preliminary stage of the reaction, these results point out that sulphate and dithionate are formed

by two different reactions, the dithionate being formed only by the reduction of weak oxidising agents, the permanganites, the primary products of reduction of permanganates.

The results of analysis of the precipitate obtained by adding aq. H_2S to ammonium permanganate solution (53 c.c., 0·5% and 1%) are recorded in Table V.

The results show that the value of the molecular ratio of $(NH_4)_2O$ (or better $2NH_3+H_2O$): MnO_2 is 1:1 instead of 1:2 which is the value for the molecular ratio of $K_2O : MnO_2$ obtained in the reduction of potassium permanganate. The composition of the compound formed may be represented as $(NH_4)_2O.MnO_2$ or $H_2O.2NH_3.MnO_2$. This abnormality in the high content of 'ammonium' may be due to the feebly basic nature of ammonium hydroxide. However, the results are remarkably in agreement with those obtained by Biltz (*loc. cit.*) who obtained the same compound by treating manganese dioxide with ammonia, cooled by a freezing mixture of solid carbon dioxide and pumping off ammonia. He represented hydrated manganese dioxide as permanganous acid, H_2MnO_3 and its normal salt, ammonium permanganite as $(NH_4)_2\,MnO_3$ (*i.e.*, $H_2O.2NH_3.MnO_2$).

The acidic properties of hydrated manganese dioxide are very feeble and as a result it shows a great tendency to form polymerides, polypermanganites (Cocosinschy, *Z. anorg. Chem.*, 1930, **176**, 186; 1930, **298**, 189). The formation of a polypermanganite may be represented thus :

$$O=Mn\left\langle\begin{matrix}OH & OH\\ OH & OH\end{matrix}\right\rangle Mn=O \longrightarrow H_2Mn_2O_5+H_2O$$

In the reduction of potassium and barium permanganates, the primary reduction products are $K_2O.\,2MnO_2$ and $BaO.\,2MnO_2$. These products may be regarded as the derivatives of polypermanganous acid, $H_2Mn_2O_5$, and their composition may be represented as $K_2Mn_2O_5$; $BaMn_2O_5$. A similar compound is obtained from calcium permanganate.

The Alkaline Stage of the Reaction

After the neutral stage, further addition of hydrogen sulphide to a permanganate solution makes the solution alkaline. Potassium, barium or ammonium in the solution is now accounted for as S_2O_3'', S_2O_6'', SO_4'' and OH' (titrated against a weak acid). The results are tabulated in Table VI (Expt. 1, 2 and 3).

TABLE VI

The products of the reaction in solution where H_2S is passed through solution of permanganates (1%, 50 c.c.) till the solution becomes alkaline

No.	Permanganate used.	$^*(SO_4)''$.	$(S_2O_3)''$.	$(S_2O_6)''$.	$(OH)'$.	K, Ba, or NH_4 calc	K, Ba or NH_4 obs.
1	$KMnO_4$	0·0905 g.	0·0160 g	0·0024 g.	0·0123 g.	0·1092 g.	0·1093 g.
2	NH_4MnO_4	0·1040	0·0060	0·0024	0·0101	0·0524	0·0524
3	$Ba(MnO_4)_2$	0·0958	0·0044	0·0025	0·0452	0·0183	0·0183
4	$KMnO_3$	Nil	0·0044	0·0023	—	—	—

* The amount of $(SO_4)''$ estimated in the alkaline stage is almost the same as observed in the neutral stage of the eaction.

The alkalinity of the solution is due to the free alkali present formed by the hydrolysis of permanganites. Dunnicliff and Nijhawan (*loc. cit.*) ascribe this to the adsorption of sulphate ions. The results (Table VI) obtained by us, however, do not lend support to this view.

The Polysulphide and the Final Stages

When increasing amounts of hydrogen sulphide are added, total potassium, barium and 'ammonium' comes in the filtrate and the solution assumes a yellow colour due to the formation of polysulphides. Some increase in the amount of thiosulphate and sulphate is noticeable due to the decomposition of dithionate which is found to be absent. The results are similar to those obtained in the reduction of calcium permanganate (Mohammad and Ahluwalia, *loc. cit.*). If hydrogen sulphide is passed for several hours even the polysulphides decompose, leaving behind a colourless solution. Barium in the final stage of the reaction is wholly accounted for as $(S_2O_3)''$ and $(SO_4)''$ and their values approximate to 5 molecules of barium sulphate and one molecule of barium thiosulphate. The results can be represented by the equation,

$$6Ba(MnO_4)_2 + 25H_2S = 5BaSO_4 + BaS_2O_3 + 12MnS + 25H_2O + 6S$$

(Calculating from the experimental value $BaSO_4$, 82·3% ; BaS_2O_3, 17·7% and the value for for the molecular ratio of $BaSO_4 : BaS_2O_3$ is 4·98 : 1).

In the case of ammonium and potassium permanganates the solution of the final stage remains alkaline. This is probably due to the following reactions :

$$(1)\ KHS + H_2O \rightleftharpoons KOH + H_2S$$

$$(2)\ K_2S + H_2O \rightleftharpoons KOH + KHS$$

(Desgre, *Compt. rend.*, 1926, **183**, 2244, 137)

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PARACHOR OF POTASSIUM DICHROMATE AND CONSTITUTION OF CHROMIC ACID

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The parachor of $K_2Cr_2O_7$ in aqueous solution has been determined. The results when compared with parachors of K_2CrO_4 and CrO_3 confirm the view that CrO_3 exists in solution mainly as $H_2Cr_2O_7$, dichromic acid.

Parachor of potassium dichromate has been determined by Sugden and Wilkins (*J. Chem. Soc.*, 1928, 263) by fusion method and the value obtained is 450·8. Lakhani and Daroga (*J. Indian Chem. Soc.*, 1938, **15**, 41) got the value 450·6 by solution method, using $P_{H_2O}=54$ and applying their formula

$$P_m = (1+x)P_p + x\frac{P_x}{2} .$$

We have shown (*J. Indian Chem. Soc.*, 1942, **19**, 226) that there is no justification for this formulae and that the correct value to be substituted for P_{H_2O} is 52·3. Introducing this correction and using the usual formula

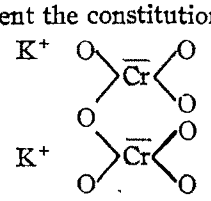
$$P_m = (1-x)P_p + xP_x$$

the value comes out to be 414 by Lakhani and Daroga's result.

We have therefore investigated the parachor of potassium dichromate at various concentrations and our results are as follows.

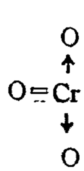
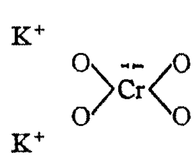
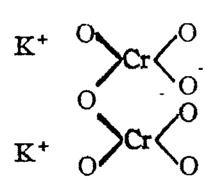
x.	M_m.	Temp.	D.	γ.	P_m.	P_x.
0·007169	19·96	20°	1·074	76·26	54·92	447·7
		30°	1·071	74·06	54·68	414·2
		50°	1·061	70·96	54·59	401·7
0·005718	19·57	22°	1·059	74·42	54·27	439·9
		30°	1·056	73·10	54·17	414·5
		40°	1·052	71·85	54·19	417·9
		50°	1·048	70·65	54 18	416·1
0·004283	19·18	22°	1·043	75·67	53·91	476·3
		40°	1·038	72·78	53·99	494·9
		50°	1·032	71·37	54·03	504·8
0·003794	19·095	30°	1·037	72·85	53·74	484·9
		40°	1·033	71·32	53·73	484·7
		50°	1·029	70·21	53·69	471·7
0 00300	18·83	20°	1·031	71·71	53·16	440·0
		30°	1·026	71·06	53·22	460·0
		40°	1·020	69·68	53·26	4680
		50°	1·015	68·22	53·28	4720

The value of parachor as calculated from atomic parachor (K=110, Cr=54, O=20) is $P_{K_2Cr_2O_7}=468$. If, however, we represent the constitution of potassium dichromate by the formula



then we have two polar linkages and four semi-polar bonds each of which has a value $=-1·6$. Hence $P_{K_2Cr_2O_7}=468-9·6=458·4$. The experimental values as obtained by us are near about these values although they vary with the concentration of potassium dichromate.

The structural formula for chromium trioxide, potassium chromate and potassium dichromate according to electronic theory of valency are

 .  . 

The corresponding values of observed and calculated parachor for them are :

	Calc.	Obs. in solution
CrO_3	134	102
K_2CrO_4	347·6	195
$K_2Cr_2O_7$	458·4	440

The lower values indicate some sort of ionisation. If CrO_3 exists in solution as H_2CrO_4 its constitution will be represented in a similar manner as K_2CrO_4 and hence it should be possible to obtain the value of CrO_3 group in solution from the values of parachor of K_2CrO_4. Unfortunately the value of $2P^K$ is alone 220 and hence it is impossible to obtain the value of CrO_3 group from $P_{K_2CrO_4}$ by the procedure

$$P_{CrO_3} = P_{K_2CrO_4} - 2P_K - P_O.$$

Even if we assume that ionic parachor of potassium is not the same as its atomic parachor, yet the results with $K_2Cr_2O_7$ in which K ions are also present, shows that it should not be very different as the calculated and observed parachors of $K_2Cr_2O_7$ are nearly the same. On the other hand from $P_{K_2Cr_2O_7}$ we get

$$2P_{CrO_3} = P_{K_2Cr_2O_7} - 2P_K - P_O = 440 - 220 - 20 = 200, \quad \text{or,} \quad P_{CrO_3} \text{ in solution} = \frac{200}{2} = 100.$$

This value nearly equals the observed value 102 in solution. The parachor observations therefore support the view that chromic acid exists in solution mainly as $H_2Cr_2O_7$ and equilibrium exists of the type $H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$.

Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1930, **7**, 913; *J. Phys. Chem.*, 1931, **35**, 2405) have determined the absorption of K_2CrO_4, $K_2Cr_2O_7$ and CrO_3 solutions, in water. Their results confirm the view that in concentrated solution CrO_3 exists mainly as $H_2Cr_2O_7$.

We have determined the conductivity of chromium tri oxide solution and calculated the values for μ_∞ from observed results assuming that CrO_3 exists in solution as $H_2Cr_2O_7$ and H_2CrO_4. We have then determined the values for μ_∞ for K_2CrO_4 and $K_2Cr_2O_7$ solutions experimentally. From these values, we calculated the values for μ_∞ H_2CrO_4 and μ_∞ $H_2Cr_2O_7$ by applying Kohlrausch law. The actual values are not very correct but they are correct enough to show that the calculated value agrees with the observed value of CrO_3 determined as $H_2Cr_2O_7$. In short the observations support the view that CrO_3 exists in solution mainly as $H_2Cr_2O_7$.

We have tried to determine coagulating power of CrO_3 assuming it to exist as $H_2Cr_2O_7$ and H_2CrO_4 and have compared it with the coagulating power of K_2CrO_4 and $K_2Cr_2O_7$ using $Fe(OH)_3$ sol. The results do not help to draw any conclusion.

The observations of Bewen and Chatwin (*J. Chem. Soc.*, 1932, 2081) on photochemical oxidation of alcohol by potassium chromate using dilute solution support the existence of $HCrO_4$ ions in dilute solutions.

The results of Koppel and Blumenthal (*Z. anorg. Chem.*, 1907, **53**, 228) on boiling points of aqueous solutions of CrO_3 and of Sherril (*J. Amer. Chem. Soc.*, 1907, **29**, 1641), Kremann (*Wein Akad. Ber.*, 1911, **120**, *ii*, *b*, 339), Buchner and Prins (*Z. physikal. Chem.*, 1913, **81**, 113) on freezing point, however support the view that CrO_3 exists mainly as H_2CrO_4.

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PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N·C·S-. PART XIV. MECHANISM OF DESULPHURISATION

By Ramchandra Sahasrabudhey and Hans Krall

Dixon's discussion of thirty years ago no longer agrees with all the facts now known and more modern view is advanced

About the year 1869 A. W. Hofmann desulphurised certain thiocarbamides with mercuric oxide (*Ber.*, 1869, **2**, 455, 600, 687). In the case of thiocarbanilide he expressed the change by the following equation :

$$(C_6H_5{\cdot}NH)_2CS + HgO \longrightarrow (C_6H_5{\cdot}NH)_2CO + HgS.$$

Weith (*Ber.*, 1874, **7**, 10) recognised the true nature of the change and showed that desulphurisation was dependent on the removal of the elements of hydrogen sulphide from a thiocarbamide. Later some more thiocarbamides were desulphurised by other workers (*vide J. Indian Chem. Soc.*, 1942, **19**, 343 for the references) using lead or copper salts as desulphurising agents and the reaction came to be recognised as represented by the equation :

$$R{\cdot}NH{\cdot}CS{\cdot}NH_2 + Pb(OH)_2 \longrightarrow R{\cdot}NH{\cdot}CN + PbS + H_2O.$$

Then followed the more extensive researches on desulphurisation by Dixon (*J. Chem. Soc.*, 1889, **55**, 618 ; 1893, **63**, 318) who like Weith considered that desulphurisation was a process which essentially consisted in the withdrawal of the elements of hydrogen sulphide from thiocarbamides. Dixon established the following conclusions :

(*i*) All monosubstituted thiocarbamides are desulphurised.

(*ii*) All disubstituted thiocarbamides, which contain at least one aryl substituent, are desulphurised.

(*iii*) Disubstituted thiocarbamides, which contain both the substituents non-aromatic, are not desulphurised.

(*iv*) Tri- and tetra-substituted thiocarbamides are not desulphurised.

On Weith's view it is at once apparent that tri- and tetra-substituted thiocarbamides cannot be desulphurised as they do not contain the two hydrogen atoms required for the removal of sulphur as H_2S. But so far any explanation of the rather unexpected behaviour of dialkyl thiocarbamides, which do not undergo desulphurisation, has been lacking. Dixon considered all thiocarbamides to have similar constitutions (*J. Chem. Soc.*, 1912, **101**, 2502). Obviously the easy desulphurisation of diaryl compounds in sharp contrast to the nondesulphurisability of dialkyl derivatives cannot be explained on any theory of the constitution of substituted thiocarbamides which assumes similar constitutions for both classes of compounds.

We think that any theory of desulphurisation of thiocarbamides should be consistent with the following observations :

(*i*) Dialkyl substituted and tri-and tetra-substituted thiocarbamides do not undergo desulphurisation,

(*ii*) Desulphurisation does not take place in a strong acid medium. It occurs almost quantitatively in alkaline media and partially also in dilute solutions of weak acids. In concentrated solutions of weak acids it is suppressed (*vide*, Part XV of this series, p. 67).

(*iii*) Salts of such metals as copper, mercury, lead and silver only are effective in bringing about desulphurisation.

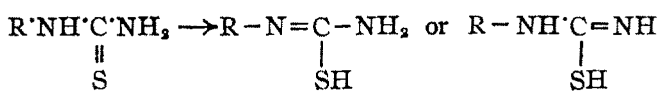
(*iv*) In contrast to the usual slowness of organic reactions in general, desulphurisation is quite a quick process and the impression that it is an ionic reaction is hard to avoid.

We suggest the following mechanism for desulphurisation:

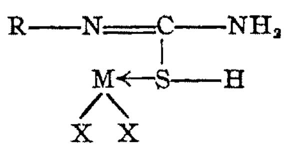
The hydroxides of copper, mercury, lead and silver are known to be active desulphurising agents. Salts of weak acids of these metals (*e.g* copper acetate) are also effective to a limited extent, but this property of these salts is probably a result of their easy hydrolysis into the corresponding hydroxides (*vide*, Part XV).

We think that the reaction is initiated by the formation of molecular compounds of thiocarbamides with the metallic bases through co-ordination at the sulphur atom. There is ample evidence for such co-ordination (*vide*, separate communication on the constitution of metal salt derivatives of thiocarbamides). Werner (*J. Chem. Soc.*, 1890, 57, 283) in his studies with the benzyl chloride derivatives of thiocarbamides showed that the S-substituted thiocarbamides yield complexes with metalic salts *e.g.*, those of platinum, mercury and gold, which decompose into such products as R. S. MX (where R is an alkyl group and MX, the metallic salt residue) and the sulphide of the metal. This explains why only the salts of the above metals are effective in bringing about desulphurisation.

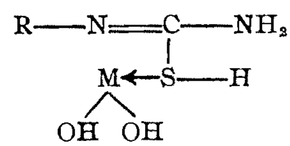
Werner, Krall and others have shown that thiocarbamides tend to assume pseudothiocarbamidic configurations in aqueous solutions, thus:



A co-ordination complex of the metallic salt MX_2 or the hydroxide $M(OH)_2$ with the thiocarbamide would therefore have the structures (I) and (II):

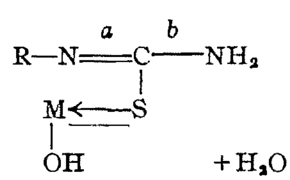


(I)

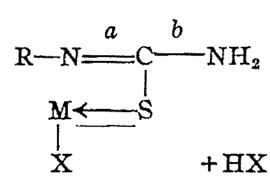


(II)

If in the metallic salt or the hydroxide the valency force between the metal and the acid or hydroxide groups be weak, as is known to be the case with divalent mercury, lead and copper, the following changes become probable:



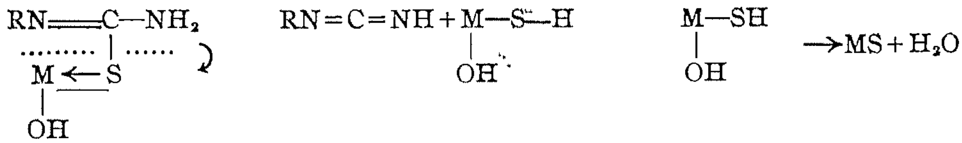
(III)



(IV)

The mobility of a second hydrogen atom from *b*-nitrogen to sulphur in (III) makes it very

unstable and it rearranges in the following manner, a carbodiimide being formed along with the metallic sulphide and water.



If a second mobile hydrogen atom be not available in (IV), the hydrogens of the amino group in some way having been deprived of their mobility or if the residue MX is stable enough, decomposition of (IV) into (V) and (VI) may occur.

$$\underset{\text{(V)}}{\begin{array}{c}R{-}N{=}C{-}NH_2\\ |\\ S\\ \oplus\end{array}} \qquad\qquad \underset{\text{(VI)}}{M{-}X}$$

(V) through some mechanism not yet fully understood in cases where R is an aromatic radical, in presence of some oxidising agent, gets oxidised to thiodiazoles.

The salts of divalent copper, mercury etc. by virtue of their easy reducibility to the lower valency states themselves can serve the purpose of such oxidising agents in acidic media, the reduced salt residues combining with unchanged thiocarbamides to form various complexes (*cf. J. Indian Chem. Soc.*, 1942, **19**, 25).

Silver nitrate is an effective desulphurising agent but it does not oxidise thiocarbamides probably because it cannot be reduced easily to a state of lower valency (*cf.* Lal and Krall, *J. Indian Chem. Soc.*, 1937, **14**, 474) like the salts of divalent copper (*cf.* the reaction of CuCl with phenylthiocarbamide, *J. Indian Chem. Soc.*, 1942, **19**, 25).

It is evident therefore from the above discussion that the mobility of a second hydrogen atom from nitrogen to sulphur is an essential condition for desulphurisation. This is supported, as already pointed out by the non-desulphurisability of the tri- and tetra-substituted thiocarbamides, whatever be the nature of their substituents. We consider that in acidic media desulphurisation is not possible because the mobility of the hydrogen of the amino or the imino group is checked through a process of salt formation which is very likely to occur under those conditions.

$$R{-}N{=}\underset{\displaystyle S{-}H}{\underset{|}{C}}{-}\overset{\oplus}{NH_3}\ \ \overset{\ominus}{X}$$

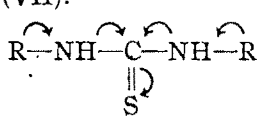
That such salt formation occurs has become sufficiently clear from our experiments with copper acetate and phenylthiocarbamide in strongly acidic boiling solutions where desulphurisation was found to be suppressed with increasing concentration of acetate ions in the medium (*vide*, Part XV). A large excess of acetate ions evidently increased the stability of the salt $R-N:\underset{\displaystyle S{-}H}{\underset{|}{C}}\cdot NH_3\cdot O\cdot COCH_3$ which in weaker acid concentrations would largely hydrolyse into acetic acid and $R\cdot N\cdot\underset{\displaystyle SH}{\underset{|}{C}}{-}NH_2$, the latter being susceptible to desulphurisation.

Action of nitrous acid in glacial acetic acid or strongly acidified solutions of phenylthiocarbamide supports the view stated above. It is found that under these conditions the amino group is not attacked but oxidation of phenylthiocarbamide

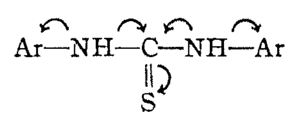
occurs, the nitroso derivative of Hector's base being obtained (*J. Indian Chem. Soc.*, 1939, **16**, 33). In dilute acetic acid solutions, however, the amino group reacts with nitrous acid to form nitrogen (Mehta and Krall, *J. Indian Chem. Soc.*, 1935, **12**, 640). The large excess of acetate ions in concentrated acetic acid solutions stabilises the ammonium salt of the acid and the amino group of the thiocarbamide. In a dilute solution, the salt $R{\cdot}N{\cdot}\underset{|}{\underset{SH}{C}}{\cdot}NH_3\ O{\cdot}COCH_3$ is largely hydrolysed into free thiocarbamide and so the amino group becomes exposed to the attack by the nitrous acid.

In a dilute solution of a strong acid the reaction follows the same course as in the concentrated solutions of weak acids. The explanation probably lies in the fact that even in dilute solutions the salts formed with strong acid are not hydrolysed into free thiocarbamide.

Nondesulphurisability of alkyl substituted thiocarbamides can also be explained on a similar reasoning. The alkyl radicals through their strongly proton attracting nature (+ I inductive effect) check the mobility of hydrogens from nitrogen to sulphur and hence no desulphurisation is possible. In a symmetrical compound the electronic displacements due to inductive effect can be shown as in (VII).



(VII)



(VIII)

In a monoalkyl derivative or in a mixed disubstituted thiocarbamide the proton attracting effect of the alkyl group being either not strong enough to hinder the mobility of the hydrogens or having been partially neutralised by the -I effect of the aryl group, desulphurisation becomes possible.

In a diaryl thiocarbamide, on the other hand, the electronic displacements can be represented as in (VIII).

The -I effect of the aryl groups facilitates proton release from the -NH- group and the hydrogens of the imino groups can tautomerise on to the sulphur, this makes such compounds easily desulphurisable.

The scheme (VII) above requires as a direct consequence of the electron displacements towards the sulphur atom that in such alkyl thiocarbamides sulphur should become strongly negatively charged. A striking confirmation of this has been obtained by Lecher (*Annalen*, 1925, **445**, 35) who has shown that the sulphur atom of the tetramethylthiocarbamide can co-ordinate a proton in proton-donating media *viz.*, acidic solutions.

It has been pointed out in a preceding paragraph that desulphurisation is quite a quick process which suggests that ionic changes take place in the reaction. A tendency towards the segregation of the electrical charges in the different zones on the molecules as postulated by the above schemes and as has been found by Kumler and Fohlen (*J. Amer. Chem. Soc.*, 1942, **64**, 1944) from their study of dipole moments would make these molecules behave very nearly as ions.

A discussion of the other peculiarities in the behaviour of aliphatic thiocarbamides, which distinguish them from their aromatic congeners, will form the subject of a separate communication.

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PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N-C-S-. PART XV. ACTION OF COPPER ACETATE ON PHENYLTHIOCARBAMIDE

By Ramchandra Sahasrabudhey and Hans Krall

The action of copper acetate on phenylthiocarbamide has been investigated. At ordinary temperatures a part of phenylthiocarbamide is oxidised to Hector's base and the cuprous acetate produced simultaneously combines with the rest of the thiocarbamide to form a complex. This is comparable with the action of other copper salts already studied. In boiling solutions, however, it is remarkable that desulphurisation to phenylcyanamide also takes place even in the presence of considerable concentrations of acetic acid.

In continuation of the earlier work (*J. Indian Chem. Soc.*, 1942, **19**, 25) the action of copper acetate on phenylthiocarbamide has been investigated with the object of studying the action of the copper salt of a weak acid.

In the case of cupric sulphate or chloride it is found that the primary reaction of these copper salts with phenylthiocarbamide, irrespective of the variations in temperature, dilution, or the p_H of the medium, so long as it continues to be acidic, is the oxidation of phenylthiocarbamide to Hector's base (*Ber.*, 1889, **22**, 1176), the copper salts being simultaneously reduced to the cuprous state. The cuprous salts so formed combine with unoxidised thiocarbamide to form various complexes depending upon the temperature of the medium. Temperature thus controls the *extent* of the primary oxidative change but the *nature* of the change remains essentially the same at ordinary as well as at boiling temperature.

In the case of copper acetate we have found that all the factors, *viz.*, p_H, dilution and temperature of the medium influence the change both in its qualitative and quantitative aspects, the desulphurisation of a thiourea in acid solution being noteworthy.

At ordinary temperatures phenylthiocarbamide reduces copper acetate and forms a white complex with the reduced salt, the part of the phenylthiocarbamide, which undergoes oxidation, giving Hector's base (*cf.* the action of $CuSO_4$ and $CuCl_2$). The reaction may be roughly represented by the following equations :

(*i*) $2Ph{\cdot}NH{\cdot}CS{\cdot}NH_2 + 4CuAc_2 \longrightarrow 4CuAc + C_{14}H_{12}N_4\dot{S} + S + 4HAc$

(*ii*) $8Ph{\cdot}NH{\cdot}CS{\cdot}NH_2 + 4CuAc \longrightarrow 4CuAc{\cdot}(Ph{\cdot}NH{\cdot}CS{\cdot}NH_2)_2$

The results of these experiments are presented below in Table I.

At higher temperature (boiling solutions) both oxidation and desulphurisation of phenylthiocarbamide proceed simultaneously ; but if an excess of free acetic acid be present in the system, oxidation is favoured at the expense of desulphurisation (*vide* Table II).

The graph in Fig. 1, shown at the end of the paper, brings out in a characteristic way the effect of increasing acid concentration on the processes of oxidation and desulphurisation.

Experimental

Set I (At the ordinary temperatures)

1·52 G. (1/100 mole) of phenylthiocarbamide were suspended in 150 c.c. of water at the ordinary temperature and 50 c.c. of saturated solution of normal copper acetate added. The mixture on being vigorously stirred developed a turbidity and phenylthiocarbamide passed into solution. It was left overnight to complete the reaction when a white amorphous precipitate

separated out. It was filtered. Hector's base was precipitated from the filtrate by neutralisation with ammonium hydroxide, dried and weighed. Unused copper remaining in the liquors was estimated iodometrically. The results are summarised in Table I.

TABLE I

At ordinary temperature.

1·52 G. (1/100 mole) of phenylthiocarbamide were used and a saturated solution of normal copper added in excess.

Expt. No	Dilution.	Conc. of acetic acid.	Copper used as CuAc for complex formation.	Hector's base isolated.
1	200 c.c.	5*N*	0·3045 g.	8·33 g.
2	200	2*N*	0·3976	0·30
3	200	*N*	...	0·28
4	200	*N*/2	0·3108	0·24
5	200	Nil	0·3076	Traces
6	1000	Nil	...	Nil

(*i*) In experiments 1 to 5 the same complex is formed. The amount of Hector's base isolated decreases from expt. 1 to 5 probably because in weaker acid solutions it is not completely retained in solution and gets precipitated along with the complex due to the hydrolysis of its acetate.
(*ii*) In experiment 5 the complex appeared to have a slightly blackish tinge
(*iii*) In experiment 6 black residue of copper sulphide was obtained instead of a complex and from the solution on concentration phenylurea was isolated.

TABLE II

In boiling solutions.

3·04 G. of phenylthiourea (1/50 mole) were used Dilution = 250 c.c.

Expt. No.	Ratio of phenylthiocarbamide : CuAc.	Medium.	Copper present (as $CuAc_2$)	Copper used up.	% of Hector's base formed	% aPhenylcyanamide formed.*
1	1 : 2	Alkaline				83·0
2	1 : 1	Pure aq.	1·2714 g.	1·2714 g.	0·0 g.	40·0
3	1 . 2	,,	2·5428	1·2570	0 0	46·0
4	1 : 1	N·NH_4Ac	1·2714	1·2700	0·0	39·1
5	,,	*N*/2HAc	,,	1·2300	<10·0	57·0
6	,,	*N* ,,	,,	1·2500	10·0-15·0	55·0
7	,,	2*N* ,,	,,	1·2700	28·0	45·0
8	,,	3*N* ,,	,,	,,	39·0	30·0
9	,,	4*N* ,,	,,	,,	48·0	17·3
10	,,	5*N* ,,	,,	,,	65·0	<15·0

* Percentages of Hector's base and phenylcyanamide are calculated on the theoretical yields from 3·04 g. of phenylthiocarbamide.

Set II (In boiling solutions).

3·04 G. (1/50 mole) of phenylthiocarbamide were dissolved in boiling water and an equivalent quantity of copper acetate in the form of a concentrated solution of known strength, also at boiling temperature, were mixed and the burner removed immediately. The quantity of water was so chosen that the total bulk of the mixture was always about 250 c.c. In experiments in which an acidic medium was used, glacial acetic acid was added in the requisite quantity before the addition of copper acetate, care being taken that the final volume of the mixture did not exceed 250 c.c. The mixture was vigorously stirred and allowed to cool to the room temperature when it was filtered. The filtrate was made up to a measured volume and from a portion of it Hector's base was precipitated with an excess of strong aqueous ammonia. It was filtered, dried and weighed. From this quantity the total amount of Hector's base formed could be calculated.

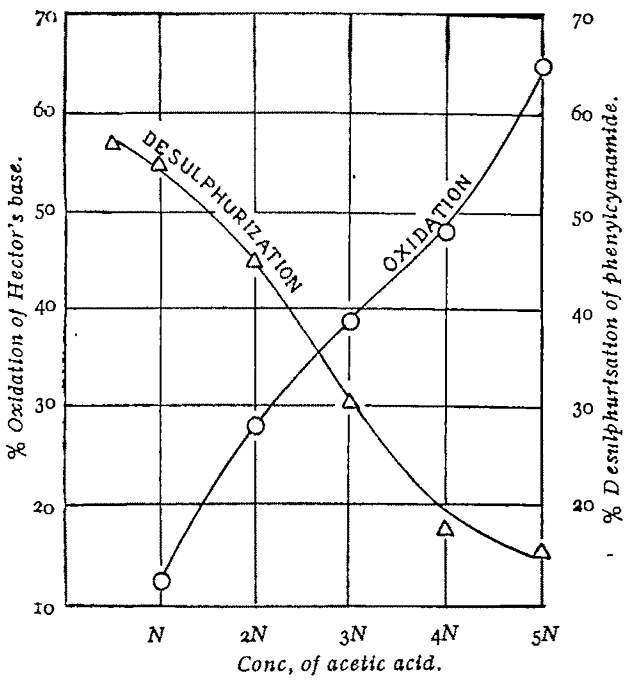
Phenylcyanamide was precipitated as the silver salt from a known volume of the liquor. The precipitated silver salt was carefully collected, washed, dried and weighed.

Phenylcyanamide was also estimated volumetrically and there was good agreement in the results. They are summarised in Table II.

DISCUSSION

Table I shows that the figures for Hector's base isolated and copper used up are both too high to be explained strictly on the equations given above. Some other complex with a lower percentage of phenylthiocarbamide is evidently formed, *e.g.*, $(Ph\cdot NH\cdot CS\cdot NH_2)\cdot CuAc$ (*cf.* reactions with other cupric salts where also a mixture of two complexes is obtained at ordinary temperatures, *loc. cit.*). Clearly the concentration of the free acid does not interfere with the course of the reaction. Experiments 5 and 6 bring out the effect of dilution. Excepting the result of experiment No. 6, where the change in the type of the reaction is owing to the hydrolysis of copper acetate on excessive dilution, the general trend at ordinary temperature is comparable with that of copper sulphate or copper chloride.

FIG. 1



In boiling hot solutions (Table II), on the other hand, desulphurisation of phenylthiocarbamide takes place simultaneously, although with an increase in the concentration of free acetic acid in the medium, the formation of Hector's base is naturally augmented at the expense of desulphurisation. This is in sharp contrast to what obtains with copper sulphate and chloride under analogous conditions. The following suggestions are tentatively put forward to explain this very different behaviour of the acetic acid salt :

(*i*) Oxidation of phenylthiocarbamide is brought about by the normal salt, desulphurisation by the hydroxide formed as a result of hydrolysis. Hydrolysis of copper acetate even in presence of considerable quantities of free acetic acid is probable in boiling solutions.

(*ii*) The formation of as much as 65% Hector's base (*vide* Table II) cannot be reconciled with the formation of a complex, and it appears that the complexes $(Ph\cdot thi)_2\cdot CuAc$ and $(Ph\cdot thi)\cdot CuAc$, if formed at all, in boiling solutions, decompose into cuprous acetate and free phenylthiocarbamide. The cuprous acetate, so formed or produced as a result of the primary oxidative change, is further reduced to metallic copper, and additional oxidation of phenylthiocarbamide takes place, the total change being represented by the following equations :

(*a*) $2Ph\cdot NH\cdot CS\cdot NH_2 + 2CuAc \longrightarrow C_{14}H_{12}N_4S + 4HAc + 2Cu + S$

(*b*) $2Cu + S \longrightarrow Cu_2S$.

It has in fact been found that while cuprous chloride and cuprous sulphate complexes are quite stable in boiling solutions, cuprous acetate complex decomposes under similar conditions.

(*iii*) It has been suggested under (*ii*) that in boiling strongly acidic solutions copper acetate is reduced to metallic copper oxidising phenylthiocarbamide. It is surprising to find that although copper acetate can thus be reduced, it fails to augment desulphurisation. The explanation probably lies in the fact that desulphurisation of a thiocarbamide requires the removal of two hydrogen atoms through their mobility on to the sulphur atom (*vide* Part XIV) which in a strongly acidic solution of a weak acid such as acetic acid, or in dilute solutions of strong acids is hindered through a process of salt formation, thus :

$$\mathrm{Ph{\cdot}N{=}\underset{\displaystyle SH}{\underset{|}{C}}{-}NH_3Ac}$$, rendering desulphurisation difficult or impossible.

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REACTIONS OF HYPONITRITES. PART I. THE ACTION OF CHARCOAL ON SODIUM NITRITE ETC.

By Trambaklal Mohanlal Oza

Hyponitrites are formed by the action of charcoal on alkali nitrites. They, however, undergo double decomposition with the carbon dioxide formed in the reaction producing the alkali carbonate and nitrous oxide.

Sodium hyponitrite decomposes at 334-36° producing sodium oxide, nitrite and nitrate and liberating nitrogen. It appears likely that oxide and nitrite are the primary products and nitrate is the secondary product formed by auto-oxidation of the nitrite. This view receives support from the products of action of charcoal on sodium nitrite and hyponitrite.

Sodium hyponitrite is extraordinarily sensitive to carbon dioxide, fixing the latter becoming itself changed into the carbonate and setting nitrous oxide free. The sensitiveness is so unusual that it removes carbon dioxide even from air where it is present only to a small extent.

While studying the action of charcoal on potassium nitrite (*J. Indian Chem. Soc.*, 1943, **20**, 267) the author detected the presence of a small amount of nitrous oxide in the slow reaction. The observation could not be substantiated as the reaction between potassium nitrite and charcoal was always violent. Interest about the observation developed, however, as this indicated the possibility of a further side reaction leading to the formation of potassium hyponitrite, as formation of nitrous oxide from the action of charcoal on other oxides of nitrogen is precluded (Shah, *J. Chem. Soc.*, 1929, 2661). As sodium nitrite melts at a comparatively low temperature (about 335°) it was thought that this substance might react with charcoal at a lower temperature and the hyponitrite, if produced, might be detected with comparative ease since sodium hyponitrite is known to decompose above 300° (Divers, *J. Chem. Soc.*, 1892, **61**, 97). Experiments have therefore been performed to substantiate the formation of nitrous oxide in the interaction and to trace its origin.

Preliminary experiments showed that the reaction started at about 300°, slowly gathered speed and became measurable at 325°. The reaction rate increased with increasing temperature and became violent at 360-65°. After the violence the reaction practically ceased. The reaction had the characteristics of a chain reaction as in the case of potassium nitrate and charcoal, starting slowly and developing speed with time at a constant temperature. An examination of the gaseous products revealed the presence of about 50 % nitrous oxide but the examination of the residue by the usual test did not indicate any hyponitrite therein.

In the present work results of experiments (*i*) at different temperature and (*ii*) with different proportions of the reactants are described. The formation of sodium hyponitrite, as an intermediate unstable product, is established by devising a method of detecting the substance based on the observation of Partington and Shah (*J. Chem. Soc.*, 1931, 2071). The thermal decomposition of sodium hyponitrite, pure and in presence of charcoal, is studied and the action of carbon dioxide on sodium hyponitrite investigated.

Experimental

Materials.—Merck's extra pure sodium nitrite was recrystallised from alcohol-water and dried. Pure charcoal was prepared from cane sugar by a combination of the methods

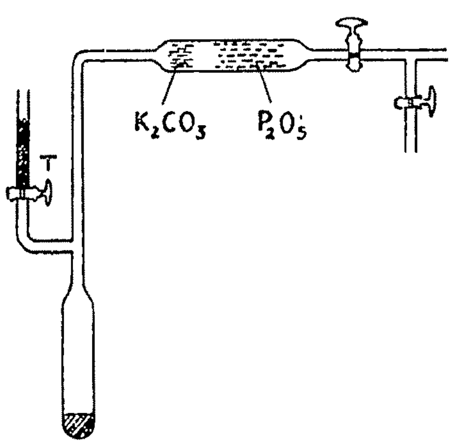
of Shah (*loc. cit.*) and King (*J. Chem. Soc.*, 1933, 843). The charcoal used in these experiments left 0·07 % ash on incineration.

Apparatus and Procedure.—A carefully weighed quantity of the reactants was heated electrically in a vacuum at the bottom of a 1 foot vertical column sealed on to the Sprengel pump with a tap in between. No KOH trap was necessary as the gas produced contained very little nitrogen tetroxide. The apparatus, tested for leaks, was evacuated by Hyvac followed by Sprengel for fifteen minutes. As the charcoal gave out adsorbed gas on commencing to heat, the apparatus was once again evacuated at 250°.

Analysis.—The gas showed nitrous oxide, nitrogen, carbon dioxide and traces of carbon monoxide and nitric oxide. These were estimated by the standard methods: nitrous oxide was absorbed out in cold alcohol saturated with nitric oxide and carbon monoxide in a nitrogen atmosphere after previously absorbing carbon dioxide in strong KOH saturated with nitrous oxide. All volumes stated are at N.T.P.

The solid residue showed no nitrate (diphenylamine test). It contained carbonate, nitrite, and hyponitrite (with probably some carbide). The hyponitrite, present only in very small amounts, was detected thus: the residue after pumping off the gas was allowed to cool to room temperature under the prevailing vacuum and about 1 c.c. water added cautiously by turning the tap T (Fig. 1). Gas was liberated and this was collected dry, by passing over a layer of potassium carbonate and phosphorus pentoxide. The analysis of this gas showed nitrous oxide and nitrogen. Partington and Shah (*loc. cit.*) observed that sodium hyponitrite produced a mixture of nitrous oxide and nitrogen on treatment with water in a vacuum. The very small amount of hyponitrite present had, probably, its colour masked in the thick precipitate due to the carbonate and the nitrite simultaneously present (with silver nitrate).

FIG. 1.



The nitrite was determined with permanganate, adding excess tetroxalate and titrating the tetroxalate excess: carbonate by weak HCl.

Effect of Temperature.—The results of experiments with sodium nitrite and 20 % (on the weight of nitrite) charcoal at different temperatures are given in Table I. The reaction was controllable up to 350°, but was violent in 5 to 6 minutes at 360° and in 3 to 4 minutes at 370°.

TABLE I

Action of charcoal on sodium nitrite at different temperatures.

Temp.	$NaNO_2$	Gas total.	% Composition of gases N_2	N_2O.	CO_2	CO.	NO.	Residue $NaNO_2$.	Na_2CO_3
325°	0·1743 g.	23·5	31·5	54·9	11·5	0·6	0·9	0·071	0·0867
340	0·1806	32·95	34·3	51·5	12·4	1·0	0·6	—	—
350	0·1803	27·5	35·2	50·0	12·0	1·5	0·7	0·0614	0·0986
360	0·1442	30·85	40·6	31·1	17·2	5·7	5·6	0·0154	0·1049
370	0·1476	26·7	45·7	25·5	17·0	6·2	6·0	0·0441	0·0895

The results show that (*i*) so long as the reaction is under control (*a*) the proportions of nitrous oxide, carbon dioxide and nitrogen are practically the same ; nitrous oxide slightly diminishing and the latter two slightly increasing with rising temperature ; (*b*) the proportions of nitric oxide and carbon monoxide are small ; (*ii*) in the violent reaction, the proportion of nitrogen increases and that of nitrous oxide diminishes, the changes being the greater, the earlier the violence setting in. The proportions of carbon dioxide, carbon monoxide and nitric oxide increase in the violent reaction, the observation being just the same as in the case of charcoal and potassium nitrite (*loc. cit.*).

As reduction in the proportion of nitrous oxide in the violent reaction tends towards the absence or abatement of the corresponding reaction in the violent stage and would, in this respect, be in complete analogy with the potassium nitrite and charcoal results, experiments were conducted by separating the gaseous products of the violent reaction. As the effect of temperature is only slight the slow reaction was begun at 340° and the evolved gas continuously pumped off and the temperature gradually raised till (after 65 min.) the violence set in (at only 355°) when the tap between the heating column and the pump was turned off and the gas on the pump side collected along with the former (*a*). The tap was next opened and the remaining gas collected separately (*b*). As the reaction immediately before violence was fairly rapid, all the gas formed before the violence could not be collected in (*a*) so that (*b*) does contain some of (*a*). Under (*c*) is given the results of another experiment with the same amounts of the reactants, the gas being allowed to accumulate in the system till (after 106 min.) the reaction ceased altogether. The results of these experiments are given in Table II.

TABLE II

Gas evolved under continuous pumping (a) before, (b) during the violent reaction and (c) when allowed to accumulate in the system.

	$NaNO_2$	Gas (total).	Percentage composition of gas N_2	N_2O	CO_2.	CO.	NO	Residue $NaNO_2$.	Na_2CO_3.
(*a*)	0·3753 g.	49·8	51·8	32·6	13·4	1·2	1·6	—	—
(*b*)		23·5	63·8	8 5	17·0	6·9	4·8	—	—
(*c*)	0·3748	77·5	52·8	31·4	13·8	0·9	1·0	0·0028g.	0·3020g.

The results show in addition to the normal features of Table I that (*i*) there is a considerable difference in the proportions of nitrous oxide and nitrogen in (*a*) and (*b*), the former being very small in the violent reaction ; (*ii*) there is little difference in the nature of gaseous products whether the gas is continuously pumped off or allowed to accumulate in the system during the reaction except that in the latter case the reaction is slower ; this shows that the reactions all occur in the solid (or molten) phase and not in the gaseous phase ; (*iii*) the effect of increase in mass of the reactants is (*cf.* Table I) to reduce the production of nitrous oxide probably by a rise in local temperature (the reactions are exothermic) which hinder the production of hyponitrite. With potassium nitrite and charcoal (*loc. cit.*) where the slow reaction occurred at about 400°, very little nitrous oxide was detected.

Effect of Mass of Charcoal.—Effect of mass of charcoal on the production of nitrous oxide was next studied by carrying out the reaction at 340° with different proportions of

charcoal. The reactions were stopped when about 10 c.c. of gas were collected. This was immaterial as will be seen by comparing Table I or II and III since the composition of the gas was practically uniform whether the extent of the reaction was small or large. These results are given in Table III and show that the effect of increasing the proportion of charcoal is similar to a rise in temperature.

TABLE III

Effect of mass of charcoal at 340°.

Charcoal.	$NaNO_2$.	Gas (total).	Percentage composition of gas N_2.	N_2O.	CO_2.	CO.	NO.
5%	0·1719 g.	4·3	41·9	46·5	9·3	2·2	1·0
20	0·1798	8·8	37·5	49·6	11·5	1·0	1·0
60	0·1800	8·4	42·5	42·0	11·0	2·5	2·0

The residue of the 60% experiment, when cold, was treated with water in order to test for hyponitrite in the manner stated before. The evolved gas was collected and examined. As the result showed the presence of nitrous oxide, experiments were performed with 10% charcoal at lower temperature (330-35°) so as to facilitate the production of hyponitrite. Two experiments were performed—one short, in which heating was done till only about 10 c.c. gas were produced and the other long where about five times as much gas was formed. The gas was removed by Hyvac and Sprengel, the residue allowed to cool to room temperature in the vacuum and then treated with water. The composition of the gas thus obtained is shown in Table IV.

TABLE IV

Gas evolved on water treatment of the cold residues in vacuo.

$NaNO_2$.	Charcoal.	% Composition of thegas Gas (total).	N_2O.	N_2 (with some combustible gas).
0·1800 g.	60% (short)	1 35	0·4	0·95
0·1803	10 (short)	1·85	1·2	0·65
0·1795	10 (long)	5·4	3·5	1·9

The results justify the belief that hyponitrite is produced in the reaction. Partington and Shah (*loc. cit.*) have shown that gas of some such composition as this is evolved when sodium hyponitrite is treated under vacuum with water. The gas, unabsorbed in alcohol, caught fire when the tube containing it was held slanting, top up, near a spirit lamp flame producing a blue flame which decended steadily but swiftly down the length of the tube occupied by the gas. The gas may not be containing hydrogen for, on admixture with air, it did not explode. It might be some hydrocarbon, mixed with nitrogen, produced by the action of water on some traces of carbide present in the residue.

Having thus proved that hyponitrite was produced in the reaction the question next was to explain as to how nitrous oxide was formed from the hyponitrite. The thermal decomposition of sodium hyponitrite has been studied by several workers and though reference books (Mellor) show that nitrous oxide is produced by the thermal decomposition of sodium hyponitrite, the work

of Divers (*loc. cit.*), Ray and Ganguli (*J. Chem. Soc.*, 1907, **91**, 1399) and Partington and Shah (*loc. cit.*) showed that the substance may not be produced from the hyponitrite by thermal decomposition. These workers have shown that nitrous oxide is one of the components of the gas produced by the thermal decomposition of cupric, alkaline earth, lead, zinc, mercury but not silver and sodium hyponitrites. Berthelot and Petit (*Compt. rend.*, 1889, **109**, 92) showed from a consideration of the heats of formation of hyponitrous acid in aqueous solution and of nitrous oxide that it was possible for sodium hyponitrite to decompose into nitrous oxide and sodium oxide. It was therefore thought worthwhile to carry out a few experiments on heating sodium hyponitrite.

Thermal Decomposition of Sodium Hyponitrite.—Pure sodium hyponitrite was prepared by the Diver's (*loc. cit.*) method (modified) to be described in Part II. It was examined for purity: (1) 0·0237 g. anhydrous substance gave 0·0260 g. NaCl; (2) 0·0298 g. anhydrous substance gave 0·0796 g. AgCl; (3) the substance contained no carbonate. (Found: Na, 43·1; N_2O_2, 55·8%; $Na_2N_2O_2$ requires Na, 43·4 and N_2O_2, 56·6%). Weighed quantities of the salt were heated in the same apparatus and in the same way as described before. As the reported temperature of the thermal decomposition of sodium hyponitrite is different according to different workers (Divers, above 300°; Partington and Shah, 260-65°) this was also determined. Above 250° temperature of the furnace was allowed to rise only very slowly, 10° in 15 minutes. The substance showed first signs of decomposition (fluctuation of mercury in the Sprengel pump) at 334-36° and decomposed suddenly in about 2 minutes thereafter. During the first two minutes the decomposition was but gradual. After the suddenness the reaction practically ceased. The gas was nitrogen (with only a trace of nitric oxide). The glass of the apparatus was corroded. The residue was yellow when cool and dissolved in water with hissing and effervescence. The results of these experiments are given in Table V.

TABLE V

Thermal decomposition of sodium hyponitrite.

Expt No.	$Na_2N_2O_2$.	Gas (N_2) N.T.P.	Residue		$3Na_2N_2O_2 = 2Na_2O + 2N_2 + 2NaNO_2$ demands		
			Na_2O.	$NaNO_2$.	N_2(N.T.P.).	Na_2O.	$NaNO_2$.
1	24·9 mg.	3·6 c.c.	9·9 mg.	9·0 mg.	3·5 c.c.	9·7 mg.	10·8 mg.
2	30·2	5·05	12·37	9·69	4·3	11·77	13·1
3	29·8	4 8	—	9 42	4·2	11·62	12·93
4	52·5	9·05	20·2	20·98	7·8	20·5	22 76
5	42·0	7·2	17·6	12·5	5·9	16·38	18·22

Divers (*loc. cit.*) and Partington and Shah (*loc. cit.*) considered the equation,

$$3Na_2N_2O_2 = 2Na_2O + 2N_2 + 2NaNO_2$$

to represent the decomposition. They did not give any analytical results in support of their statement. The above results show that the reaction is not so simple. The equation represents, most probably, the primary stage in the decomposition soon followed, under the prevailing conditions, by auto-oxidation of the nitrite. The latter reaction would reduce the amount of nitrite and increase the amounts of oxide and nitrogen in accordance with the above results. In all the above residues the presence of nitrate noticed also by Divers (*loc. cit.*) was distinc (diphenylamine test) and further a trace of nitric oxide was always present in the gas and

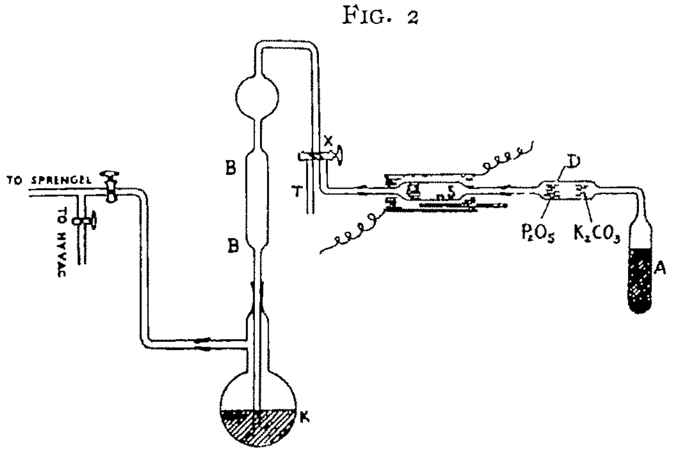
all this was to be expected if a part of the sodium nitrite underwent thermal decomposition (Ray, *J. Chem. Soc.*, 1905, **87**, 107 ; Oza and Shah, *J. Univ. Bom.*, 1942, **11**, *iii*, 70).

The action of charcoal on sodium nitrite, studied in order to see if nitrous oxide was produced in the reaction, also confirmed the above view regarding the thermal decomposition of sodium hyponitrite. Using 50 mg. of the salt and 10 mg. of charcoal the reaction was performed in the same apparatus. It occurred at 340-42° and was also sudden. The volume of gas given off was 8·9 c.c. at N.T.P. of which less than 0·1 c.c. was carbon dioxide and the rest was nitrogen with a trace of nitric oxide. The glass tube was little corroded in this reaction. The residue contained Na_2CO_3, 0·0238 g., Na_2O, 0·00914 g. and $NaNO_2$, 0·00374 g. The reaction products were thus the same as with sodium nitrite (Tables I, II and III) except that here there was no nitrous oxide and no free carbon dioxide. The existence, in the residue of such a large proportion of carbonate shows that carbon dioxide was produced in the reaction, *i.e.*, sodium nitrite had decomposed.

Having thus been baffled in tracing the cause of production of nitrous oxide the production of the gas could not be attributed to some sort of interaction between charcoal and oxides of nitrogen under the experimental conditions. The isosterism of nitrous oxide and carbon dioxide and the possibility that the latter might displace the former from sodium hyponitrite seemed to be more plausible in this case. Literature was not of much help. Kirschner (*Z. anorg. Chem.*, 1898, **16**, 424) noted that barium hyponitrite was decomposed by carbon dioxide and Divers (*loc. cit.*) found calcium hyponitrite stable to it. Partington and Shah (*loc. cit.*) stated that the alkaline earth salts were all stable in air or carbon dioxide but that sodium hyponitrite, when left exposed to air, did not give the characteristic canary yellow precipitate with silver nitrate after a fortnight. They did not, however, trace the cause of such a behaviour. The author investigated the behaviour and was surprised to find the extraordinary ease with which carbon dioxide, streamed in a vacuum over sodium hyponitrite, displaced most of the nitrous oxide of the latter at room temperature in a couple of minutes. The residue was sodium carbonate requiring twice the volume of a standard strong acid with methyl orange as with phenolphthalein.

Action of Carbon Dioxide on Sodium Hyponitrite.—The apparatus used is shown in Fig. 2. A weighed quantity of the substance was kept at **S** near a padding of glass wool in a tube the ends of which were connected by ground glass joints to a 3-way tap **X** on one side and the drying tube **D** on the other. The tube **D** was sealed on to **A** containing sodium bicarbonate to produce carbon dioxide. The tap **X** lead to Sprengel through an internal seal and a bulb **K** containing strong KOH. The empty space **BB** allowed the solution in **K** to rise when required in making adjustments and **T** allowed air to be admitted at the end of experiment and facilitated glass blowing (removing the cock and plugging the ends). The KOH solution used was previously saturated with nitrous oxide and kept in vacuum for a day while testing for leak in the

FIG. 2



apparatus. Bubble formation or rise of solution in **K** indicated leak and whenever a leak was found, the substance **S** was removed and replaced by a fresh one. The results of these experiments are given in Table VI. In experiment (*i*) temperature of the furnace was raised, after the liberation of gas in the cold ceased, to 350° and a little more gas thus collected in the pump. The experiment (*ii*) was done only in the cold. Practically all the gas was absorbed out in cold alcohol on standing. The unabsorbed gas in experiment (*i*) was evidently nitrogen produced during the heating stage. The residue was sodium carbonate mixed with a little nitrite in (*i*) and hyponitrite in (*ii*). Whenever free hyponitrite was present, together with sodium carbonate in the residue the titration reading with methyl orange was a little over two times that with phenophthalein.

TABLE VI

Streaming of carbon dioxide over sodium hyponitrite in vacuum

No.	$Na_2N_2O_2$.	Vol. of gas given off.	Composition of gas: N_2O.	N_2	Na_2CO_3 formed.
(*i*)	30 mg.	6·3 c.c.	5·6	0·7	28·1 mg.
(*ii*)	57	11·34	11·3	0·0	54·3

The great sensitivity of sodium hyponitrite to carbon dioxide is exemplary and this renders the preparation and preservation of the substance and also its handling extremely difficult. This will be described in Part II but it may be stated here that practically the whole of the substance becomes spoiled during the glass blowing stage of setting the apparatus if blowing is not done through soda lime. In this connection the results of one of the spoiled experiments may be interesting. 27·8 Mg. of the hyponitrite were inserted in the heating column, the latter sealed on to the Sprengel and the apparatus evacuated. On heating no reaction occurred even though the temperature was raised to 450°. The apparatus was left in the same state overnight. Next day about 1 c.c. of gas was formed and the residue gave Na_2CO_3, 0·02663 g. and $NaNO_2$, 0·0044 g.

CONCLUSION

The indications of these experiments are:

1. Sodium (alkali) hyponitrite is formed, to an appreciable extent, by the reducing action of charcoal on sodium (alkali) nitrite. Its production is low at higher temperatures and under conditions tending to raise the local temperature of the reacting mass.

2. The action of charcoal on alkali nitrites consists of two reactions going on side by side (*i*) thermal decomposition of the nitrite, accelerated by charcoal, proceeding as:

$$(i)\quad 2(2NaNO_2 \rightleftharpoons Na_2O + NO + NO_2) \qquad \ldots \quad \mathrm{I}$$
$$2C + 2NO_2 = 2CO_2 + N_2 \qquad \ldots \quad \mathrm{II}$$
$$C + 2NO = CO_2 + N_2 \qquad \ldots \quad \mathrm{III}$$
$$2(Na_2O + CO_2 = Na_2CO_3) \qquad \ldots \quad \mathrm{IV}$$
$$\overline{4NaNO_2 + 3C = 2Na_2CO_3 + CO_2 + 2N_2}$$

the reactions (Oza and Shah, *J. Univ. Bom.*, 1942, **9**, 70; *J. Indian Chem Soc.*, 1943, **20**, 261) bringing about auto-oxidation of sodium nitrite being completely eliminated (no nitrate) as the

nitrogen oxides formed in (I) react quantitatively with charcoal as in (II) and (III); (*ii*) reduction of the nitrite to hyponitrite and production of nitrous oxide from the latter as:

$$(ii) \quad 2NaNO_2 + C = Na_2N_2O_2 + CO_2 \qquad \ldots \quad V$$

$$Na_2N_2O_2 + CO_2 = Na_2CO_3 + N_2O \qquad \ldots \quad VI$$

Reaction (VI) occurs at room temperature. This explains why (1) sodium hyponitrite is not obtained from the nitrite by the use of charcoal as a reducing agent, and (2) sodium hyponitrite becomes spoiled on standing by exposure to air; (3) sodium hyponitrite undergoes decomposition at 334-36°, probably primarily according to the Diver's equation:

$$3Na_2N_2O_2 = 2Na_2O + 2N_2 + 2NaNO_2,$$

which appears to be followed under the existing conditions, by the reactions attending the auto-oxidation of the produced nitrite as:

$$2NaNO_2 \rightleftharpoons Na_2O + NO + NO_2 \qquad \ldots \quad (a)$$

$$3NaNO_2 + NO + NO_2 = 3NaNO_3 + Na_2O + N_2 \qquad \ldots \quad (b)$$

$$5NaNO_2 = Na_2O + 3NaNO_3 + N_2 \qquad \ldots \quad VII$$

This view receives support from the action of charcoal on the hyponitrite.

In view of (3) above it may be argued that in (2) the hyponitrite is the primary product. This, however, cannot be so, for such a case demands the production of larger amounts of carbon dioxide in the earlier stages of the reaction than in subsequent ones. Experiments do not indicate larger proportion of carbon dioxide where the extent of the reaction is small (Table III) than where it is large (Tables I and II).

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STUDIES ON ADSORPTION IN RELATION TO CONSTITUTION. PART III. ADSORPTION OF CARBOHYDRATES FROM AQUEOUS SOLUTIONS BY CHARCOAL

By B. P. Gyani

Adsorption of a large number of carbohydrates by charcoal from aqueous solution has been studied. The adsorption constants have been shown to be distinctive of the different families of sugars. A comparison of the adsorption data with physical and chemical properties of the molecules has been made to throw some light on the nature of attachment of the solute to the solid adsorbent.

Occasional observations on adsorption of sugars by charcoal have been recorded since over a century (Wallace, *Pol. J.*, 1871, **201**, 159; Mott, *Ber.*, 1880, **13**, 1147; Morton, *J. Amer. Chem. Soc.*, 1914, **36**, 1832). An examination of the literature, however, shows that the different carbohydrates have never been studied as regards their adsorption under similar conditions, and no attempts have been made to trace any connection between the constitution of the sugars and their adsorption. In the present investigation the general features governing the adsorption of carbohydrates under comparable conditions have been studied and an attempt has been made to correlate adsorption with the constitution of the carbohydrates.

EXPERIMENTAL

Ten simpler saccharides, viz. arabinose, dextrose, galactose, laevulose, maltose, mannose, raffinose, rhamnose, sucrose and xylose were studied. A sample of Merck's animal charcoal, with an ash of 1·5% showed good adsorptive capacity and was used as the adsorbent in these experiments. Stock solutions ($M/25$) were prepared and diluted to different concentrations as required.

The method adopted for the estimation of the carbohydrates was one of direct weighing. Shallow cups of aluminium foil, 6 cm. × 4 cm. × 1 cm. were prepared, weighing about 0·3 g. each and were numbered. They were placed inside a small electrically heated oven and 5 c.c. of the experimental solution introduced into them. The temperature was then raised but was not allowed to exceed 60°. When the water had all evaporated, which took about 3 to 4 hours, the heating was continued for another half an hour (at 100° for hydrated sugars), after which the cups were withdrawn and immediately weighed. Preliminary experiments with known solutions showed that the estimations were correct to within 1% in the case of most of the sugars and to within 2% in the case of hydrated sugars.

The charcoal, previous to use, was heated to 200° under vacuum; 20 c.c. of the experimental solution were taken in each experiment, in well stoppered bottles with 2 g. of the charcoal and were maintained at 30° in a thermostat with occasional shaking for 72 hours. After the end of the experiment the solution was centrifuged and the clear solution was analysed. No filter papers were used. The experimental results are recorded in Tables I and II. Except where otherwise stated all concentrations are expressed as gram mols ($\times 10^5$).

The adsorption of some more carbohydrates was also studied under similar conditions, and the results are recorded in Table II. The concentrations are in g. per 5 c.c.

TABLE I

		Arabinose.					*Xylose.*					*Dextrose.*		
Initial conc.	Equil. conc.	x/m.	Log c.	Log x/m.	Initial conc.	Equil. conc.	x/m.	Log c.	Log x/m.	Initial conc.	Equil. conc.	x/m.	Log c.	Log x/m.
20·00	8·20	11 80	0·9138	1·0719	20·13	8·00	12·13	0·9031	1·0838	20 05	7·83	12·22	0·8938	1·0871
17·00	7·00	10·00	0 8451	1·0000	17·00	6·70	10 30	0·8261	1 0128	15 20	5 39	9·81	0·7316	0·9917
10·93	4·53	6·40	0·6561	0·8062	10·60	4·00	6·60	0·6021	0·8195	10·22	3·22	7·00	0 5079	0 8451
6·66	2·80	3·86	0·4472	0 5866	6·66	2·33	4·33	0·3674	0·6365	6·66	1·94	4·72	0·2878	0·6739
5·00	2·13	2·87	0·3284	0·4579	4 90	1·60	3·30	0·2041	0·5185	5 00	1·33	3·67	0·1239	0·5647
		Galactose.					*Laevulose*					*Mannose.*		
20·05	7·22	12·83	0·8585	1·1082	20·11	8·11	12·00	0·9090	1·0792	20·05	6·88	13·17	0·8376	1·1200
15·90	5·41	10·49	0·7332	1·0207	16·03	6·01	10·02	0·7789	1·0008	17·40	5·72	11·68	0·7574	1·0675
10·28	2·83	7·45	0·4518	0·8722	10·22	3·22	7·00	0·5079	0·8451	10·17	2·83	7·34	0·4518	0·8657
6·66	1·61	5·05	0·2068	0·7033	6·72	1·94	4·78	0·2878	0 6794	6 66	2 00	4·66	0·3010	0·6684
5·00	1·33	3·67	0·1239	0·5647	5·00	1·33	3·66	0 1239	0·5635	5·00	1 33	3·66	0·1239	0·5635
		Rhamnose.					*Sucrose*					*Maltose.*		
20·00	4·16	15·84	0·6191	1·1998	5·00	0·32	4·68	−0·4949	0·6702	5·00	0·24	4·76	−0·6198	0·6776
15·62	3·22	12·40	0·5079	1·0934	6 66	0·35	6·31	−0·4559	0·8000	6·66	0·29	6·37	−0·5376	0·8041
9·94	2·07	7·87	0·3160	0·8960	9·99	0·71	9 28	−0·1487	0 9675	10·00	0·59	9·41	−0·2291	0·9736
6·65	1·22	5·43	0·0864	0·7348	14·22	1 22	13·00	0·0864	1·1139	14·13	1·11	13·02	0·0453	1·1145
5·00	0·85	4·15	0·0706	0·6180	19·47	2·44	17·03	0·3874	1·2311	19·50	2·43	17·07	0·3856	1·2321

TABLE II

Carbohydrates.	Initial conc.	Equil. conc.	%Adsorption.
Dextrin	0·0250	0·0018	92·8
Inulin	0·0250	0·0024	90·4
Maltin	0·0250	0·0000	100·0
Starch	0·0250	0·0008	96·8
α-Methyl d-glucoside	0·0250	0·0026	89·6
Raffinose	0·0446	0·0006	98·7

DISCUSSION

An examination of the data clearly shows that active charcoal has considerable adsorptive power for the different sugars. Measurements showed that the adsorption of the various sugars on silica gel was generally less than 2%, which was negligible compared to the 55 to 95% adsorption shown by charcoal. In this respect the behaviour of the two adsorbents are quite different.

Fig 1. shows the plots of x/m against equilibrium concentrations for the different sugars. The isotherms thus obtained are located in a regular order. Thus at the bottom of the figure we have the two pentoses, arabinose and xylose, having adsorption coefficients of about 57% and 66% respectively. Proceeding upwards we come across the hexoses, dextrose, fructose, mannose and galactose, which all lie close together in a bunch. The adsorption coefficients of the hexoses lie between 70 to 75%. The isotherms of the pair of bioses lie at the top and run close to one another. The adsorption coefficients of the bioses are distinctly higher and have a value approximating 88%. The methyl pentose, rhamnose, with an adsorption coefficient of

80% comes midway between the hexoses and the bioses. Two regular features emerge from the above data. Firstly the adsorption increases in a general way with increasing molecular weight of the solute. Secondly sugars of the same family form distinct groups of adsorption isotherms. The adsorption coefficients of the various sugars of the same family lie close together and increase in regular steps as one passes from the pentoses to the bioses.

The behaviour of rhamnose is somewhat anomalous. It may be regarded either as a methyl pentose or a reduced hexose. Although its molecular weight (164) is less than that of the hexoses (180), it shows a larger adsorption. Further the isotherm for rhamnose differs from those of the hexoses which have a characteristic concave form, but is more akin to the isotherms of the pentoses which are more or less rectilinear over the concentrations studied. Though similar in form, the isotherm for rhamnose differs from those of the pentoses in as much as it is located much higher than any of the pentoses.

FIG. 1

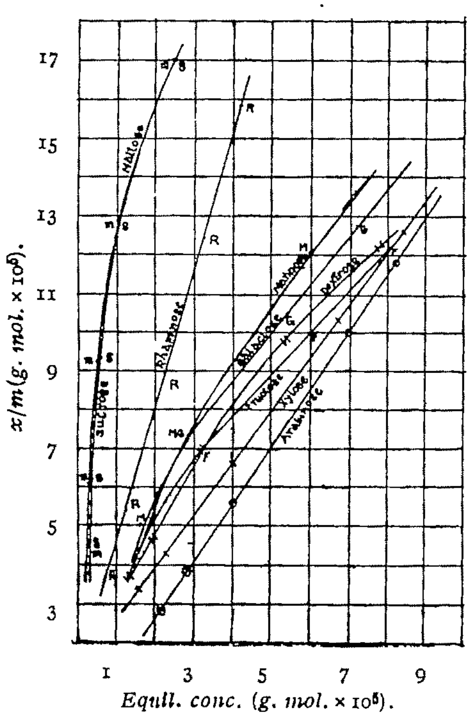
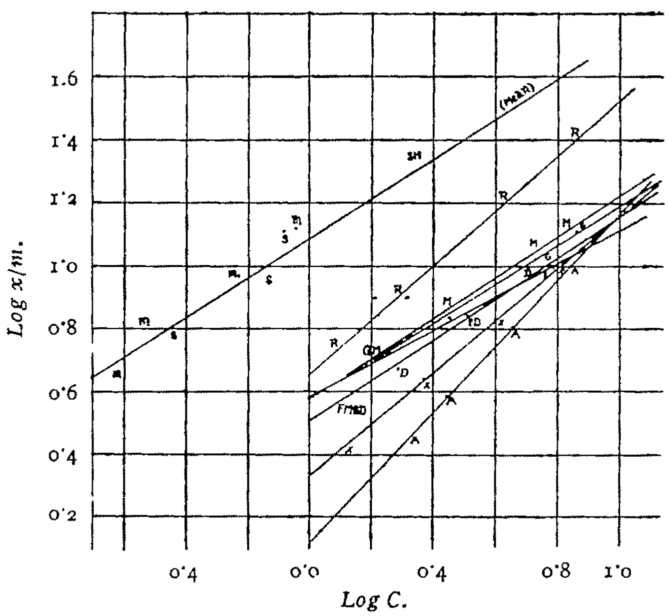


FIG. 2



[A = arabinose; X = xylose; D = dextrose, F = fructose; G = galactose; M = mannose; R = raffinose; S = succrose; m = maltose]

In Fig. 2, the plot of log x/m against log c have been given. The plots are all straight lines which shows that the usual adsorption equation $x/m = \alpha c^{\frac{1}{n}}$ is generally obeyed. From Fig. 2, the values of α and $1/n$ have been calculated in the usual manner, and are given in Table III. A comparison of these values again clearly brings out the family relationship of the sugars with regard to adsorption.

TABLE III

Substance	Arabinose	Xylose	Dextrose	Galactose	Mannose	Fructose	Rhamnose	Maltose	Sucrose
$1/n$ ...	1·054	0·820	0·652	0·613	0·641	0·531	0·870	0·605	0·605
α ...	1·288	2·188	3·166	3·758	3·758	3·802	4·467	12·30	12·30
Melting point ...	159°	144°	146°	166°	195°	95°	93°	110°	165
Period of osazone formation (min.)	10	7	5	15 to 19	1½	2	9	...	30
No of hydrates ...	Nil	Nil	one	Nil	Nil	Nil	one	one	one

The pentoses including rhamnose have values of $1/n$ approximating 1. The hexoses have almost a constant value with a mean of 0·635, whilst the bioses have a mean value of 0·605. It is interesting to note that fructose, the only keto-hexose studied, has a somewhat lower value of 0·531. The value of α increases in a general way with increasing molecular weight of the sugar.

The adsorption of a number of polysaccharides is given in Table II. It will be seen that the adsorption coefficients are all high and conform to the general rule that adsorption increases with increasing complexity (*cf.* Rosenthaler, *Arch. Pharm.*, 1907, **244**, 259; Michaelis and Rona *loc. cit.*).

The adsorption of α-methyl *d*-glucoside (89·6%) may be compared with that of glucose (64%) at about the same concentration and also of the tri-saccharide raffinose (98·7%) with the bioses (about 94%), further confirming the above rule.

In Table III, the melting points, the period of formation of osazone (Mulliken, "Identification of Pure Organic Compounds," Vol. I, pp. 29-30) and the existence of hydrates where they occur, have been recorded. It will be seen that there is no simple relationship between melting point and constitution of the sugar. Linner and Gortner (*J. Phys. Chem.*, 1935, **39**, 35) observed during the adsorption of saturated fatty acids on charcoal a parallel fluctuation of adsorption and melting point with odd and even members of the series. On this basis they pointed out that the adsorbed molecules may be in a solid state *i.e.* a sort of crystallisation may take place on the surface. In the present experiments no such behaviour has been observed.

The period of formation of osazones vary with the constitution of sugars but beyond a very general connection no rigid regularity can be observed. The formation of hydrates appears to be quite a specific property of the sugars. It is thus remarkable that inspite of the lack of any regularity between the physical and chemical properties of the sugars and their constitution, the adsorption data should have a neat family relationship. One may therefore conclude that although chemical constitution does play a part in the process of adsorption, the resulting attachment between the adsorbent and the solute is not so intimate as to be affected by the detailed structure of the molecule. In other words the attachment must be even looser than in compounds such as hydrates. Further work is in progress.

In conclusion the author wishes to thank Dr. P. B. Ganguly for his guidance and Principal K. Prasad for laboratory facilities.

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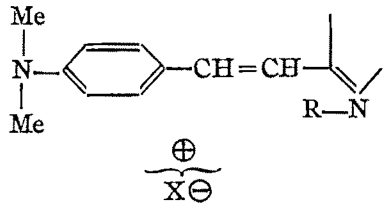
SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF p-DIETHYLAMINOBENZALDEHYDE WITH APPROPRIATE HETEROCYCLIC COMPOUNDS. PART I

By M. Q. Doja and Muktdeo Pandey

Three new dyestuffs have been obtained by the condensation of *p*-diethylaminobenzaldehyde with the ethiodides of lepidine, *p*-toluquinaldine and 6-ethoxyquinaldine One of these compounds, the *p*-toluquinaldine condensation product has been found to be a powerful sensitiser which can be commercially utilised. Unlike other cyanine dyes, these shbstances dye silk and wool in fast colours. The flourescence and other characteristics of these dyes have also been examined and recorded.

Cyanine dyes with two methenyl groups between the two ring systems (Doja, *Chem. Review*, 1932, **11**, 293) generally conform to the formula (A) and are prepared by the condensation of *p*-dimethylaminobenzaldehyde with heterocyclic ammonium compounds possessing a



when R = an alkyl radical.
X = an acid radical.

(A)

reactive methyl group (Konig *J. prakt. Chem.*, 1912, **86**, 166; Barbier, *Bull. Soc. Chim.*, 1920, **28**, 427; Mills and Smith, *J. Chem. Soc.*, 1922, **121**, 2736; Hamer, *ibid.*, 1929, 2598; 1930, 995; König, *Ber.*, 1928, **61**, 2065). On account of the fact that some of the dyestuffs belonging to this series are marked sensitisers (Mills and Pope, *J. Chem. Soc.*, 1922, **121**, 946) it was considered of interest to investigate the nature of compounds produced in the above reaction by the use of *p*-diethylaminobenzaldehyde in place of the *p*-dimethylamino compound. The present work was undertaken with this object in view (*cf.* B. P. 449527; also see Cocker and Turner, *J. Chem. Soc.*, 1940, 57). In making a choice of the heterocyclic compounds, which are to be condensed with the aldehyde, we have given preference to those which were constituents of commercially valuable sensitisers. Thus (1) *p*-toluquinaldine, a constituent of the well known orthochromatic sensitiser "pinaverdol" (Wise, Adams, Stewart and Lund, *Ind. Eng. Chem.*, 1919, **11**, 460; Mills and Pope, *Phot. J.*, 1920, **60**, 183; D.R.P. 167159, 167770, 158078, 170048, 170049) and "orthochrome T" (D. R. P. 154475, 127771); (2) 6-ethoxyquinaldine, a constituent of the German commercial product "pinachrome", and (3) lepidine, a constituent of the deep and infra-red sensitisers "kryptocyanine" and "neocyanine" (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661; Hamer, *J. Chem. Soc.*, 1927, 2801) have been selected in the first instance. The ethiodides of these bases have been condensed with *p*-diethylaminobenzaldehyde in absolute alcoholic solution with piperidine as a catalyst, and the resulting compounds are found to possess unusual sensitising characteristics. As will be evident from the wedge spectrograms (Kenneth, Mees and Wratten, *Brit. J. Phot.*, 1907, 384) recorded in Fig. 1, the lepidine condensation product, 4-*p*-diethylaminostyrylquiuoline ethiodide (E) does not confer any extra sensitisation on the photographic plate. On the other hand the condensation product

of p-toluquinaldine, 2-p-diethylaminostyryl-6-methylquinoline ethiodide (F) is a powerful sensitiser, the zone of additional sensitisation extending up to λ 6700. In this respect it surpasses even the famous orthochromatic sensitiser "pinaverdol" and very nearly equals to the panchromatic sensitiser "pinacyanol" (Mills and Pope, *Phot. J.*, 1920, **60**, 253; Hamer, *J. Chem. Soc.*, 1927, 2796; D R.P. 172118, 175034, 178688, 189942, 200207). It may be noted, in this connection, that the band of extra sensitisation is not only extensive but intense, which fact enhances the value of the compound as a practical sinsitiser. For commercial purposes we have named this sensitiser "Sensitine P". The condensation product of 6-ethoxyquinaldine, 2-p-diethylaminostyryl-6-ethoxyquinoline ethiodide (G) is a week sensitiser, the faint band of extra sensitisation reaching up to λ 6300. The general characteristics of the wedge spectrograms of all the three compounds are summarised in Table I.

TABLE I

Compound.	Total range of sensitisation.	Range of uniformly intense sensitisation.	Extra sensitisation. Maxima.	Extra sensitisation. Minima.
(E)	3800-5200Å	4400-4800Å	nil	nil
(F)	3900-6700Å	5100-6400Å	5600-6200Å	5050-5850Å
(G)	3850-6300Å	5200-5900Å	5550Å	5800Å

TABLE II

Compound.	Colour produced on Wool.	Silk.	Cotton.
(E)	Violet	Sapphire blue	Weak blue-black.
(F)	Maroon	Deep amethyst	Reddish blue
(G)	Deep pink	Reddish violet	Deep violet

Cyanine dyes generally produce pretty but fugitive shades on cotton, wool, and silk. The compounds now synthesised, however, appear to be exceptions (*cf.* U.S P. 1524791 and E.P. 232740). They not only dye silk and wool in beautiful colours but the shades thus produced are fairly resistant to both sunlight and washing. The shades on cotton are poor and easily removed. It appears that these substances are more suitable for the dyeing of wool than silk, because the shades in the former case are faster. In Table II are recorded the shades produced on wool, silk and cotton from a neutral bath.

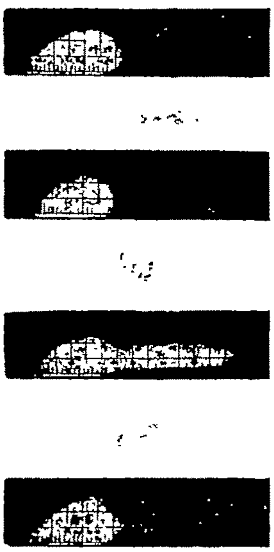
All the three compounds are soluble in water and chloroform, readily so in alcohol and insoluble in ether. Their melting points, crystalline properties and optical characteristics are given in Table III. In column 4 the "form" of the crystal is expressed as euhedral, subhedral, or anhedral, according as the crystal shows well developed partly developed or not at all developed external faces, under a microscope.

TABLE III

Compound.	Shape.	Habit.	Form.	Streak.	M.p.	Colour in ordinary light.	Colour through transmitted light.	Reflex.	Pleochroism. Colour of light in one position of polariser.	Pleochroism. Colour after rotation through 90°.
(E)	Irregular earthy crystals	Nil	Anhedral	Blue	159°	Brownish black	Deep violet	Nil	Brinjal blue	Weak, light violet
(F)	Microscopic needles	Acicular	Subhedral	Reddish violet	221	Rust-red	Claret red	Moderate light green	Dark red	Strong light orange yello[illegible]
(G)	Small glistening plates	Tubular	Euhedral	Reddish violet	218	Sage green	Smoky green	Strong, emerald green	Greenish white	Stron[illegible] opaque

Being cyanine dyes, the solution of these substances exhibits the characteristic property of the discharge of colour by the addition of mineral acids and its restoration by caustic alkalis. In this connection Mills and Pope (*Phot. J.*, 1920, **44**, 255) noted that alcoholic solutions are more resistant to decolourisation than aqueous solutions. So far as these newly prepared dyes are concerned, as will be seen from Table IV, the case is opposite. It is the aqueous solutions which require larger quantities of acid for decolourisation (*cf.* Doja and Prasad, *J. Indian Chem. Soc.*, 1943, **20**, 154).

FIG. 1.



Unbathed Plate

(E)

(F)

(G)

It is interesting to note here that the difference in the quantity of acid required for the aqueous and alcoholic solutions goes hand in hand with the sensitising power of the dye. The toluquinaldine condensation product (F) which has the maximum sensitising power has also got the largest difference; on the other hand (E) with practically no sensitising power has the smallest difference.

Weak solutions of these dyestuffs in rectified spirit (1 : 50,000) exhibit flourescence, which is given in Table V. The method of recording the flourescence is the same as described by Doja (*J. Indian Chem. Soc.*, 1940, **17**, 348).

TABLE IV

Compound.	Volums in c.c. of $N/100$ HCl required for decolourisation of 2 c.c. of 1 : 10,000. Aqueous solution		Alcoholic solution.	
(E)	3·0, 3·1	3·05	2·2, 2·2	2·2
(F)	15·4, 15·4	15·4	3·2, 3·3	3·25
(G)	4·7, 4·6	4·65	1·1, 1·2	1·15

TABLE V

Wallace colour filter No.	Colour of the flouorescent beam seen at right angles to the incident beam. (E)	(F)	(G)
1	Dark blue (seen with difficulty)	Weak yellow (seen with difficulty).	Very faint pink
2	Weak yellowish blue.	Yellowish red	Weak yellowish blue.
3	Blue	Reddish yellow	Red
4	Bluish red	Yellow	Yellowish red
5	Yellowish green	Greenish yellow	Yellow
6	Green	Greenish yellow	Reddish yellow
7	Faint blue	Light absorbed	Light absorbed
8	Light absorbed	Light absorbed	Light absorbed
9	Light absorbed	Weak blue (seen with difficulty)	Reddish blue
10	Greenish yellow	Crimson	Yellowish red

EXPERIMENTAL

Streak.—The "streak" of the crystal was determined by rubbing it on a piece of white unglazed porcelain Streak Plate and noting the colour of the powder.

4-p-*Diethylaminostyrylquinoline-ethiodide*.—A solution of lepidine ethiodide (1·7 g.), *p*-diethylaminobenzaldehyde (1 g.) and piperidine (0·3 c.c.) in 30 c.c. of absolute alcohol was refluxed for a couple of hours. On cooling earthy crystals separated out which were recrystallised from absolute methyl alcohol, yield 1·6 g. (61·5%). (Found: I, 27·71. $C_{23}H_{27}N_2I$ requires I, 27·73 per cent).

2-p-*Diethylaminostyryl-6-methylquinoline-ethiodide*.—*p*-Diethylaminobenzaldehyde (1 g.) *p*-toluquinaldine ethiodide (1·7g.), piperidine (0·5 c.c.) and absolute alcohol (36 c.c.) were heated together in a flask under reflux for 1½ hours. The solution turned violet and after leaving overnight was filled with tiny reddish needles. These were filtered off and recrystallised from methyl alcohol, yield 2·5 g. (92·5%). (Found: I, 27·12. $C_{24}H_{29}N_2I$ requires I, 26·90 per cent).

2-p-*Diethylaminostyryl-6-ethoxyquinoline-ethiodide*.—A solution of *p*-diethylaminobenzaldehyde (1 g.), 6-ethoxyquinaldine ethiodide (1 g.), piperdine (0·6 c.c.) and absolute alcohol (40 c.c.) was briskly boiled for 2 hours. The separated crystals were recrystallised from methyl alcohol, yield 2·4g. (82·7%). (Found: I, 25·32. $C_{25}H_{31}ON_2I$ requires I, 25·29 per cent).

We wish to express our gratitude to Professor L. M. Chatterjee of the Physics Department of this College for help in recording wedge spectrograms.

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PATNA.

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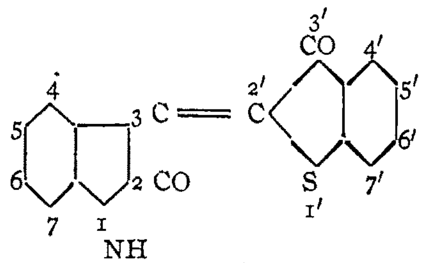
INDIGOID VAT DYES OF THE ISATIN SERIES. PART IV. 3-INDOLE-2'-(7'-METHYL) THIONAPHTHENE-INDIGOS

By Sisir Kumar Guha

3-Indole-2'-(7'-methyl)-thionaphthene-indigos, having various types of substituents in the indole part of the molecule, have been prepared. These dyestuffs have been compared with the corresponding compounds belonging to the 4'-, 5'- and 6'-methyl series. The study of the various indole-(methyl)-thionaphthene-indigos having a methyl group in every theoretically possible position of the thionaphthene nucleus is now made complete and a generalisation is made with regard to the colour and the chemical constitution of these vat colours of the isatin series, as far as one Me group is concerned.

It is also observed that this generalisation is applicable to a symmetrical dye, thioindigo and all its isomeric dimethyl derivatives. The possibilities of using a number of dyes of this indole-(methyl) thionaphthene-indigo series on a commercial basis has been suggested.

With a view to investigating into the relation between the colour and the chemical constitution of thioindigoid vat dyes of asymmetrical structure, 3-indole-2'-thionaphthene-indigo (I), commercially known as Thioindigo Scarlet (Bezdzik and Friedländer, *Monatsh*, 1908, **29**, 376 ; E.P., 17162/06) which is a typical example of a vat dye composed of two dissimilar nuclei, was chosen and the influence of one CH_3 group in 4', 5', and 6' position of the thionaphthene nucleus of this dye and its different kinds of substituted products was studied in Parts I, II and III of this series (Guha and Basu-Mallick, *J. Indian Chem. Soc.*, 1934, **11**, 395 ; Guha, *ibid.*, 1937, **14**, 240 ; 1938, **15**, 501)



(I)

This paper now deals with the preparation and a study of the various properties of 3-indole-2'-(7'-methyl)thionaphthene-indigos obtained by the condensation of 7-methyl-3-hydroxythionaphthene, recently prepared by the author (Guha, *J. Indian Chem. Soc.*, 1939, **16**, 221 ; 1943, **20**, 38) with 5-chloro-, 5-bromo-, 5 : 7-dibromo-, 5-bromo- 7-nitro-, and 5 : 7-dinitro-isatin respectively. The parent compound was previously described (Guha, *loc. cit.*). A detailed study in this series of compounds has been made by the author [2-(4-, 5-, 6-, 7-methyl) thionaphthene-acenaphthylene-indigos. Guha, *J. Indian Chem. Soc.*, 1933, **10**, 682 ; 1936, **13**, 94 ; 1938, **15**, 23 ; 1943, **20**, 37].

These 7'-methyl dyes are dark red, violet-red and violet crystalline substances. They are all soluble in pyridine and nitrobenzene. The dibromo compound is insoluble in alcohol and the rest are sparingly soluble in the same solvent. The chloro, bromo, and dibromo-dye dissolve in cold concentrated sulphuric acid producing a light green solution in each case : the bromo-nitro ; and the dinitro-substance produce a green solution when treated similarly. All of them behave similar to the isomeric 4'-, 5'-, and 6'-methyl compounds when heated above their melting points.

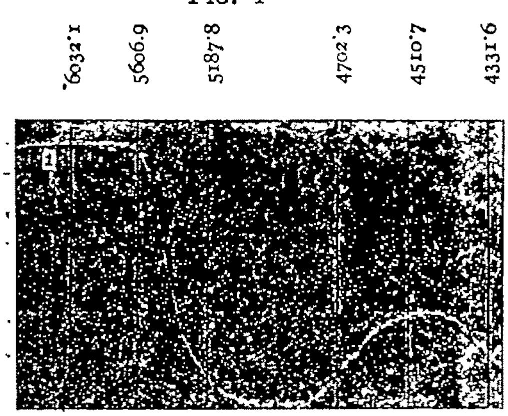
Their dyeing shades are uniformly developed on cotton from an alkaline hydrosulphite vat, the colour of which also resembles that which was found in the case of the corresponding

4′-, 5′-, and 6′-methyl substances. They have also imparted true shades on wool from a dilute sulphuric acid bath. As the dyes of this series possess a darkish tinge, their real depth of colour with respect to those of the isomeric 4′-, 5′- and 6′-methyl dyes could be only understood easily by examining them at first in xylene solution and finally confirming by taking the absorption spectra of some of them and calculating the absorption maxima (Table I) from the microphotograms of the spectra of the same(Figs. 1, 2). It is noticed that these dyes are lighter than those of the corresponding compounds of the 4′-, 5′- and 6′-methyl series.

This result also points to the conclusion that the presence of substituents e.g. Cl, Br, NO_2 etc., either alone or duplicated or combination of two different groups in the indole part of the dye, has no influence in altering the generilisation deduced before by the anthor taking only the parent compound of this series into consideration *i.e.* the depth of colour of all the isomeric indole-(methyl) thionaphthene-indigos, the detailed study of which was fully done, may now be arranged in the following order : 5-methyl dye >4-methyl dye >6-methyl dye >7-methyl dye. The position of the depth of the colour of the parent dye is next to that of the 5-methyl dye (Table I).

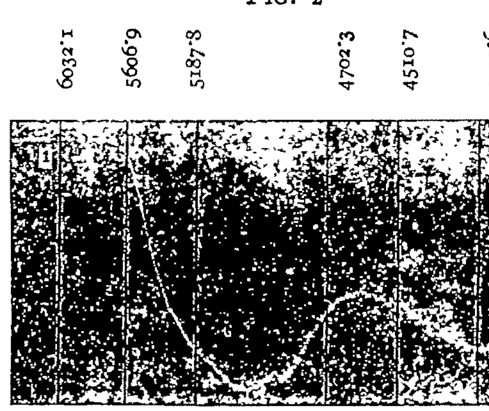
Next the author in order to find out the depth of colour of thioindigo and all its isomeric dimethyl derivatives, which are important instances of vat dyes of symmetrical structure, and to compare their relationship with those of the vat dyes of symmetrical structure, the isomeric indole-(methyl)thionaphthene-indigos under discussion, studied the 4:4′-, 5:5′-, 6:6′-dimethyl-thioindigos (Fig. 4 and Table II, *J. Indian Chem. Soc.*, 1938, **15**, 506). The 7:7′-dimethyl-thioindigo was also prepared and its properties examined (Guha, *J. Indian Chem. Soc.*, 1943, **20**, 39). Now its absorption spectrum was taken and the absorption curve drawn. It will appear that this curve (Fig. 3) also shows two maxima analogous to its isomeric substances. From the colour and the absorption maxima (Table II) it is found that the

FIG. 1



Curve 1 refers to 3-(5:7-dibromo) indole-2′-(7′-methyl)-thionaphthylene-indigo.

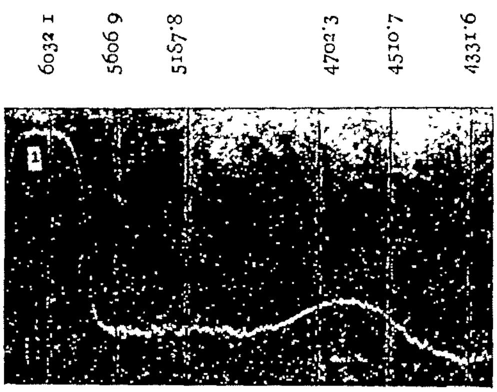
FIG. 2



Curve 1 refers to 3-(5:7-dinitro) indole-2′- (7′-methyl)-thionaphthylene-indigo

7:7′-dimethylthioindigo is the lightest of all in this series. Therefore, it may be summarised that the depth of colour of thioindigo and all its isomeric dimethyl products stand in the same relationship as to those of the indole-thionaphthene-indigo and its isomeric methyl substituted dyes (Table I and II). That is, the same generalisation with regard to the colour and the constitution is applicable to both the classes of vat dyes studied here.

FIG. 3



Curve 1 refers to 7·7′- dimethyl-thioindigo.

As the result of the syntheses of a large number and variety of isomeric indole-(methyl) thionaphthene-indigos (Parts I, II, III and IV), valuable dyestuffs of red, blood-red, scarlet-red, deep red, dark red reddish violet and violet shade have been obtained. They are characterised by their individual distinctive shade and according to choice the dyestuff may be selected for use. It is observed that the introduction of a halogen atom in the indole part of the dye gradually deepens the colour and the brightness is decreased : and that of NO_2 group further deepens the colour. Moreover, the presence of NO_2 group greatly increases the solubility of the dye in the alkaline hydrosulphite vat and enhances the affinity for cotton fibre.

The scarlet-red dye, 3-indole-2′-(5′-methyl) thionaphthene-indigo is brilliant, pleasant and deeper than 3-indole-2′-thionaphthene-indigo (Thioindigo Scarlet R). The deep red dye, 3-(5:7-dibromo) indole-2′(5′-methyl) thionaphthene is also deeper than 3-(5:7-dibromo) indole-2′-thionaphthene-indigo (Ciba Red G) (Table I). The dyeing shades of these two above mentioned dyestuffs, 3(5-iodo)indole-2′(5′-methyl) thionaphthene-indigo, 3-(5:7-dibromo) indole -2′(6′-methyl)-thionaphthene-indigo, 3-(5- bromo-7-nitro) indole -2′(4′-, 5′-, 6′-, 7′-methyl) thionaphthene-indigos and 3-(5:7-dinitro) indole-2′-thionaphthene-indigo together with all its isomeric methyl derivatives are very attractive. They may receive technical application soon on account of their depth of colour, beautiful characteristic shade and also fastness.

Finally, it may be stated that the author's attempt to establish a complete relationship between the colour and the chemical constitution of the various isomeric indole-(methyl) thionaphthene indigos and of dimethylthioindigos has been amply realised. In the thioindigoid series, a complete generalisation of this type, as far as one substituent is concerned, has been deduced now for the first time.

The future line of work in this series will be to examine how far this generalisation is applicable to 3-indole-2′-thionaphthene-indigo having different types of substituents present in every theoretically possible position of the thionaphthene nucleus of the dye. Work in this direction is being undertaken.

TABLE I

T = Thionaphthene-indigo.

Compounds.	Absorption maxima.
3-(5 :7-Dibromo) indole-2′-T	4915 Å
3-(5 :7-Dibromo) indole-2′(4′-Me) T	4910
3-′5 :7-Dibromo) indole-2′(5′-Me) T	4998
3-(5 :7-Dibromo) indole-2′(6′-Me) T	4897
3-(5 :7-Dibromo) indole-2′(7′-Me) T	4830
3-(5 :7-Dinitro) indole-2′-T	4950
3-(5 :7-Dinitro) indole-2′(4′-Me) T	4945
3-(5 :7-Dinitro) indole-2′(5′-Me) T	5070
3-(5 :7-Dinitro) indole-2′(6′-Me)T	4927
3-(5 :7-Dinitro) indole-2′(7′-Me)T	4905

TABLE II

Compounds.	Absorption maxima Longer.	Shorter
Thioindigo	5250 Å	5028 Å
4 .4′-Dimethylthioindigo	5248	5025
5 :5′-Dimethylthioindigo	5615	5296
6 :6′ Dimethylthioindigo	5295	4936
7 :7′-Dimethylthioindigo	4940	4350

EXPERIMENTAL

3-(5-*Chloro*) *indole-2'(7'-methyl)-thionaphthene-indigo*.—This dye separated from the red-brown solution, obtained by dissolving 5-chloro-isatin (0·544 g.) and 7-methyl-3-hydroxy-thionaphthene (0·492 g.) in 50 c.c. of boiling glacial acetic acid, on treatment with conentrated hydrochloric acid (3 c.c.) and heating for 20 minutes. The fine, small, stout, dark-red needles (0·827 g.) were collected, washed with acetic acid and hot water. It was crystallised from a mixture of nitrobenzene and xylene (1:3) in dark red needles melting above 300°. It is difficultly soluble in xylene and acetic acid, sparingly soluble in chloroform. It dyes cloth in dark red shade from an alkaline hydrosulphite vat and wool in the same colour from an acid bath. (Found : Cl, 10·58. $C_{17}H_{10}O_2N\,ClS$ requires Cl, 10·83 per cent).

3-(5-*Bromo*) *indole-2'-(7'-methyl)-thionaphthene-indigo* was similarly obtained as dark-red small needles from a boiling solution of 5-bromo-isatin (0·678 g.) and 7-methyl-3-hydroxy-thionaphthene (0·492 g.) in glacial acetic acid (50 c.c.) and concentrated hydrochloric acid (3-4 c.c.). The new product (1·003 g.) was crystallised from xylene in dark red needles melting above 295°. The solubility of this dye and its dyeing shade on cotton and on wool resemble those of the chloro compound. (Found : Br, 21·47. $C_{17}H_{10}O_2NBrS$ requires Br, 21·51 per cent).

3-(5:7-*Dibromo*) *indole-2' (7'-methyl)-thionaphthene-indigo* was prepared by boiling a solution of 5:7-dibromo-isatin (0.61 g.) and 7-methyl-3-hydroxythionaphthene (0·328 g.) in 65 c.c. of glacial acetic acid and 3 c.c. of concentrated hydrochloric acid for 25 minutes. The dark red needle-shaped substance (0·7915 g.) was crystallised from nitrobenzene in soft wooly clusters of needles melting above 310°. It is soluble in xylene, sparingly soluble in acetic acid, insoluble in chloroform. It dyes cotton in deep red shade from an alkaline hydrosulphite vat and wool in blood-red shade from an acid bath. (Found : Br, 35·33. $C_{17}H_9O_2\,N\,Br_2\,S$ requires Br, 35·47 per cent).

3-(5-*Bromo-7-nitro*) *indole -2'-(7'-methyl)-thionophthene-indigo*.—The solution of 5-bromo-7-nitro-isatin (0.813 g.) and 7-methyl-3-hydroxythionaphthene (0·492 g.) in 70 c.c. of hot glacial acetic acid on treatment with 5 c c. of concentrated hydrochloric acid gave a lumpy mass of the condensed product in violet-red shining wooly needles. Glacial acetic acid (30 c.c.) was further added and the solution boiled for 20 minutes. The dye (1.128 g.) was crystallised from a mixture of xylene and nitrobenzene (4:1) in dark violet-red needles melting above 305°. It is moderately soluble in xylene, sparingly soluble in acetic acid and chloroform. It imparts a dark red shade to cloth from an alkaline hydrosulphite vat and a reddish violet shade to wool from an acid bath. (Found : Br, 18 82. $C_{17}H_9O_4N_2BrS$ requires Br, 19·18 per cent).

3-(5:7-*Dinitro*) *indole-2'-(7'-methyl)thionaphthene-indigo* was prepared by heating 5:7-dinitro-isatin (0·474 g.) and 7-methyl-3-hydroxythionaphthene (0·328 g) in 40 c.c. of glacial acetic acid and concentrated hydrochloric acid (3 c c.) for 20 minutes. The violet crystalline precipitate (0·688 g.) was collected, washed with acetic acid and hot water. It was crystallised from pyridine in fine wooly needles not melting below 315°. It is sparingly soluble in xylene, acetic acid and chloroform. It dyes cloth in dark red shade from an alkaline hydrosulphite vat and wool in dark violet shade from an acid bath. (Found : S, 7.91. $C_{17}H_9O_6N_3S$ requires S, 8·35 per cent).

The author's thanks are due to Mr. Kamta Prosad, I. E. S. and Dr. R. C. Ray, D.Sc. for their interest in this piece of work and to Messrs. D. K. Bhattacharya, M.Sc. and L. M. Chatterji, M.Sc. for help with spectograph and microphotometer.

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DYES DERIVED FROM ACENAPHTHENEQUINONE. PART IX. ISOMERIC (METHYL)THIONAPHTHENE-ACENAPHTHYLENE-INDIGOS

By Sisir Kumar Guha

The relation between the colour and the chemical constitution of all the isomeric (methyl)thionaphthene-acenaphthylene-indigos has been deduced

In Part VIII of this series (Guha, *J. Indian Chem. Soc.*, 1943, **20**, 37) the preparation of a few 2-(7-methyl)thionaphthene-8′-acenaphthylene-indigos was described. But their depth of colour and subsequently their relations with those of the corresponding isomeric dyes of the 4-, 5-, and 6-methyl series (Guha, *ibid.*, 1933, **10**, 682; 1936, **13**, 94; 1938, **15**, 23) were not established which was the primary object with which the investigation was at first undertaken.

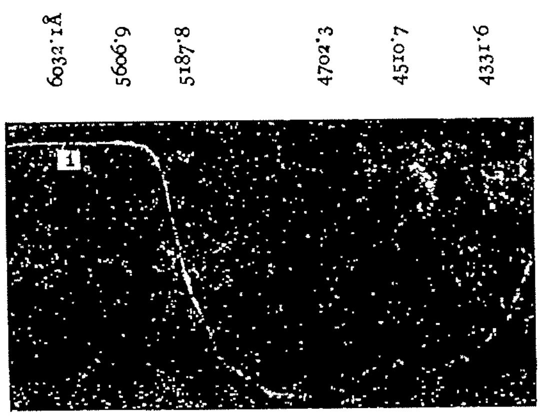
Now the absorption spectra of the parent compound of this 7-methyl series and its methoxy derivative have been taken. The absorption curves (Figs. 2 and 3) have been drawn by a microphotometer and their absorption maxima calculated. For the purpose of a comparative study, Ciba Scarlet G has also been prepared, its absorption curve (Fig. 1) drawn and the absorption maxima found. A comparison of colour and of the dyeing shades of the vat dyes of this 7-methyl series and Ciba Scarlet G and of the absorption maxima of some of these with those of the corresponding isomeric 4-, 5-, and 6-methyl compounds indicates that the influence of Me group in the 7-position of the thionaphthene nucleus of Ciba Scarlet G is also to produce "hypsochromic effect" (Table I). Moreover, it is evident that there are three positions, namely, 4-, 6-, and 7- in the thionaphthene ring of Ciba Scarlet G where the effect of substitution by Me group is to lighten the colour of the mother compound and the maximum lightening effect is produced by substitution in 6-position. But there is only one position, *viz.*, 5, where similar substitution produces "bathochromic" effect.

Therefore, the depth of colour of the various isomeric (methyl) thionaphthene-acenaphthylene-indigos may be now arranged in the order : 5-methyl dye > 4-methyl dye > 7-methyl dye > 6-methyl dye. The depth of colour of the parent compound, Ciba Scarlet G is next to that of the 5-methyl dye. The author has not taken into consideration the values against shorter absorption maxima as it is quite clear from the colour and the dyeing shades of these 7-methyl dyes that each of them is deeper in colour than the corresponding compound belonging to the 6-methyl series and this view has been confirmed by the quantitative measurement of the depth of colour of some of these dyes.

It may be pointed here that the author's observation with regard to the relation between the depth of colour and the constitution of all the isomeric (methyl)thionaphthene-acenaphthylene-indigos is not exactly the same as what was noticed in the case of another series of asymmetrical dyes, the isomeric indole-(methyl) thionaphthene-indigos and also the symmetrical dyes, the isomeric dimethylthioindigos, where the maximum lightening effect is produced by Me substitution in the 7-position of the thionaphthene ring of the molecule of the dye (Guha, *J. Indian Chem. Soc.*, 1944, **21**, 87). But, in all the three series, the general observation is the same in the sense that there is only one position in the thionaphthene ring where the introduction of the Me group produced deepening effect and three different positions where similar substitution lightened the colour of the parent compound.

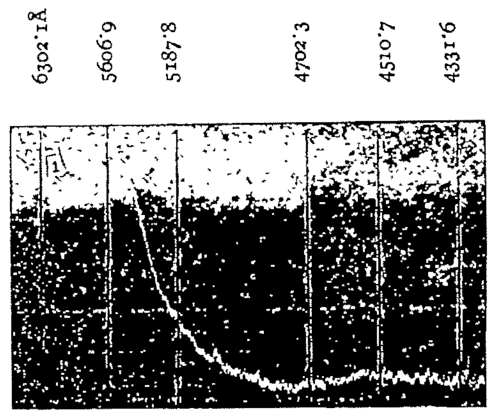
On an examination of the absorption curves of Ciba Scarlet G and the various isomeric (methyl)thionaphthene-acenaphthylene-indigos (Figs. 1, 2, and 3 ; also see Part VI of this series) it will appear that the absorption bands in the case of 5-methyl compounds which are the deepest

FIG. 1



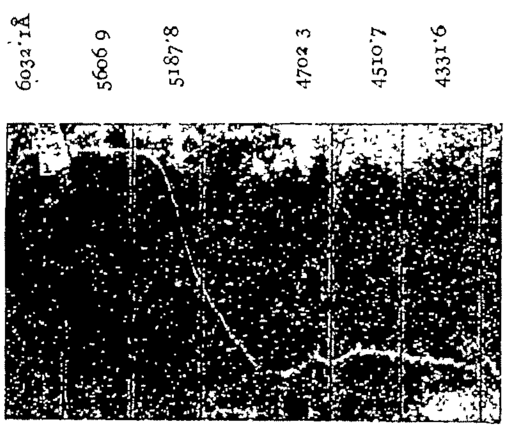
Curve 1 refers to 2-thionaphthylene-8-'acenaphthylene-indigo (Cuba Scarlet G).

FIG. 2



Curve 1 refers to 2-(7-methyl)-thionaphthylene-8′-acenaphthylene-indigo

FIG. 3



Curve 1 refers to 2-(7-methyl)-thionaphthylene-8′-acenaphthylene-indigo.

of all in this series are much broader and their depth of absorption is also greater than that of the 4-, 7-, and 6-methyl isomerides. The head of the absorption band of the 5-methyl-dye is shifted much towards the red end of the spectrum and then follow those of the 4-, 7-, and 6-methyl compounds respectively. This is in agreement with the conclusion drawn qualitatively.

It is also noticed that of the different substituents present in the acenaphthene part of the molecule of the dye, the inert group, OMe deepens the shade of the dyes more than Cl or Br atom. But this value of the methoxy dyes is marred by the fact that they offer much resistance to reduction in the hydrosulphite vat in consequence of which their true shades could not be obtained on cotton by repeated trial.

The detailed study in this acenaphthenequinone series has enabled the author to select a few vat colours of deep but pleasant and attractive shade and good fastness.

TABLE 1

T = Thionaphthene ; A = Acenaphthylene-indigo.

Compounds.	Absorption maxima.	Compound.	Absorption maxima.
2-T-8′-A (Ciba Scarlet G)	... 4775 Å	2-(4-Methyl)-T-8′-(1′-methoxy)-A	... 4810Å
2-(4-Methyl)-T-8′-A	... 4735	2-(5-Methyl)-T-8′-(1′-methoxy)-A	... 4995
2-(5-Methyl)-T-8′-A	... 4985	2-(6-Methyl) T-8′-(1′methoxy)-A	... 4783
2-(6-Methyl)-T-8′-A	... 4622	2-(7-Methyl)-T-8′-(1′-methoxy)-A	... 4790 (longer) 4685 (shorter)
2-(7-Methyl)-T-8′-A	... 4710 (longer) 4350 (shorter)		

The author's thanks are due to Messrs. D. K. Bhathacharya, M.Sc. and L. M. Chatterjee, M.Sc., for help with spectrograph and microphotometer.

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EFFECT OF COBRA (*NAJA NAJA*) VENOM AND ITS CONSTITUENTS ON THE SYNTHESIS OF ACETYLCHOLINE BY THE BRAIN CELLS OF THE RATS AND PIGEONS

BY B. N. GHOSH, S. S. DE AND N. K. SARKAR

Effect of cobra venom and some of its active principles on the synthesis of acetylcholine by the brain cells of rats and pigeons, suspended in oxygenated phosphate-Locke-glucose medium has been studied. Results indicate that cobra venom inhibits the synthesis of acetylcholine.

It has now been well established by the researches of Quastel and co-workers (*Biochem. J.*, 1936, **30**, 1668; 1938, **32**, 243; 1939, **33**, 822) and Stedman and Stedman (*ibid.*, 1937, **31**, 817) that acetylcholine is synthesised by the brain cells of animals. Quastel and co-workers (*loc. cit.*) report that the substance is formed partly in a free state and partly in a complex form and that the synthesis occurs best in the presence of glucose and oxygen. Stedman and Stedman (*loc. cit.*), however, maintain that glucose has no appreciable influence on this synthetic process. The importance of acetylcholine in the transmission of nerve impulse makes it desirable to study the effect of cobra venom on its synthesis by animal tissues. Gautrelet and Corteggiani (*Compt. rend. Soc. biol.*, 1938, **207**, 456) state that cobra venom can bring about a rapid decomposition of the acetylcholine complex with the liberation of free acetylcholine. In this paper the results of investigation on the effect of cobra venom and some of its active principles on the synthesis of acetylcholine by the brain cells of the rats and pigeons have been recorded.

EXPERIMENTAL

Immediately after the animal was killed its brain was removed and minced and, divided into a number of approximately equal parts. Weighed quantities of the minced brain were put into a number of conical flasks of the Warburg respiratory apparatus and to each of them were added 3·0 c.c. of phosphate-Locke solution containing 1 in 7000 eserine sulphate. The composition of the phosphate-Locke solution used was:—NaCl, 0·13M; KCl, 0·002M; $CaCl_2$, 0·001M; phosphate buffer p_H 7·4, 0·03 M. The flasks were fitted to the manometers, filled with oxygen and placed in a bath at 37°. The experiment lasted for 2 to 3 hours and during this period the flasks were continually shaken. When the experiment was completed the p_H of the solution in the flask was brought to 3·0 for the decomposition of the acetylcholine complex as suggested by Quastel and co-workers (*loc. cit.*). and after 30 minutes the content of the flask was neutralised and the acetylcholine estimated by measuring the contraction of the dorsal muscle of the leech. The muscle isolated from the leech was immersed in 7·0 c.c. of a saline solution of the following composition:—NaCl, 0·71%; KCl, 0·032%; $CaCl_2$, 0·0118%; $NaHCO_3$, 0·012%; glucose, 0·77%.

Oxygen was bubbled through the solution at a steady rate. The muscle with one end attached to a hook and the other to a lever by means of a silk thread, was allowed to stand in a slightly stretched condition in the oxygenated saline medium for about an hour. 0·01 Mg. of eserine sulphate was then added to the solution and after about 15 minutes this eserinised solution was removed. The muscle was washed once with the saline medium and again allowed to stand immersed in 7·0 c.c. of the oxygenated saline solution for nearly two hours to attain

a steady condition. The solution (0·1 to 0·3 c.c.), the acetylcholine content of which was to be estimated, was added and the contraction was recorded on a slowly revolving smoked drum by the lever attached to the muscle. The muscle was washed with the saline medium after each contraction and allowed to regain its original length before the next measurement was started. Contractions produced by known quantities of acetylcholine chloride were also measured and from a comparison of these data with those of the unknown, the acetylcholine content of the latter was calculated.

Effect of Cobra Venom

The venom used in the following experiments was extracted from the monocellate variety of cobra and dried as soon as possible after extraction in a vacuum desiccator over fused calcium chloride. The minimum lethal dose of the dry venom for a pigeon (390 g. to 320 g.) was 0·1 mg. The results are recorded in Table I. The estimated value of acetylcholine chloride is expressed in γ per gram of wet tissue and the data under the condition (E) give the amount of total acetylcholine present in the tissue at the commencement of the experiment. It has been observed by us that the contraction of the dorsal muscle of the leech by acetylcholine is in no way affected by the presence of cobra venom in the doses used.

From a comparison of the data under the conditions indicated in (A), (B), (C) and (D) it will be noticed that glucose strongly favours the synthesis and that cobra venom in the doses of 2 to 4 m.l.d. markedly inhibits the formation of acetylcholine by the brain tissues of rats and pigeons. The extent of inhibition is greater, the higher the dose of venom used.

TABLE I

The brain tissue was minced at about 0°, thoroughly mixed and divided into a number of approximately equal parts.

Expt.	Species of brain.	Treatment.	Period of incubation.	Total acetylcholine chloride.
1.	Pigeon	(A) One part brain, 3·0 c.c. phosphate-Locke eserine (1 :7000) solution	2 hrs.	2·90 γ/g.
		(B) Same as in (A) but glucose (0·02 M) added to the solution	2	8·75
		(C) Same as in (B) but cobra venom 0·2 mg added to the solution	2	4·25
		(D) Same as in (B) but cobra venom 0·4 mg added to the solution	2	3·40
		(E) Same as in (A)	0	1·80
2	Pigeon	(A) One part brain, 3·0 c.c phosphate-Locke eserine (1 :7000) solution	2	2·60
		(B) Same as in (A) but glucose (0·02M) added to the solution	2	9·60
		(C) Same as in (B) but cobra venom 0·2 mg added to the solution	2	5·76
		(D) Same as in (B) but cobra venom 0·4 mg added to the solution	2	4·00
		(E) Same as in (A)	0	1·86
3.	Pigeon	(A) One part brain, 3·0 c.c. phosphate-Locke eserine solution	2	2·44
		(B) Same as in (A) but glucose (0·02M) added to the solution	2	8·50
		(C) Same as in (B) but cobra venom 0·2 mg. added to the solution	2	4·86
		(D) Same as in (A)	0	1·50
4.	Rat	(A) One part brain, 3·0 c.c. phosphate-Locke eserine solution	2	2·70
		(B) Same as in (A) but glucose (0·02M) added to the solution	2	10·80
		(C) Same as in (B) but cobra venom 0·2 mg. added to the solution	2	5·64

Effect of Neurotoxin (R)

A neurotoxin was isolated from cobra venom by Ghosh and De (*Indian J. Med. Res.*, 1941, **29**, 367). This neurotoxin was weight for weight 16 times more active than the original venom and was found to be responsible for the failure of the respiratory movement. It has therefore been denoted as neurotoxin (R); the suffix (R) indicating that it affects the respiratory system. The minimum lethal dose for pigeons of this toxin was 0·0065 mg. The results are recorded in Table II. It will be noticed from the data that this neurotoxin in doses of 2 to 3 m. l. d. has very little effect on the synthesis of acetylcholine by the brain tissues of rats and pigeons.

TABLE II

The brain was minced at about 0°, thoroughly mixed and divided into a number of approximately equal parts.

Expt.	Species of brain	Treatment	Period of incubation.	Total acetyl choline chloride.
1.	Pigeon	(A) One part brain, 3 0 c.c. phosphate-Locke eserine (1 :7000) solution	0 hrs.	1·55 γ/g
		(B) Same as in (A) but glucose (0·02*M*) added to the solution	2	8·42
		(C) Same as in (B) but neurotoxin (R) 0·013 mg. added to the system	2	7·90
2	Pigeon	(A) One part brain, 3 0 c.c. phosphate-Locke eserine (1 · 7000) solution	0	1·04
		(B) Same as in (A) but glucose (0·02*M*) added to the solution	2	6·40
		(C) Same as in (B) but neurotoxin (R) 0·02 mg. added to the system	2	6·40
3	Pigeon	(A) One part brain, 3·0 c.c phosphate-Locke eserine (1 · 7000) solution	0	2·00
		(B) Same as in (A) but glucose (0·02*M*) added to the solution	2	7·40
		(C) Same as in (B) but neurotoxin (R) 0·013 mg. added to the system	2	6·90
4.	Rat	(A) One part brain, 3 0 c.c. phosphate-Locke eserine solution	2	8 80
		(B) Same as in (A) but neurotoxin (R) 0·013 mg. added to the system	2	7 85

Effect of the Inhibitor of Glycolysis and Respiration

It has been observed by us that cobra venom contains an active principle which inhibits respiration and the formation of lactic acid from glucose by the brain cells of pigeons. We have succeeded in partially separating the active principle from the crude venom. Assuming that cobra venom contains this inhibitor and the neurotoxin in the proportion of 100 : 100 the sample which we have isolated contains the two active principles in the proportion of 100 : 13. This sample is therefore considerably richer in the inhibitor of glycolysis and

respiration than the original venom. The results obtained by using this fraction are recorded in Table III. It will be noticed that this fraction containing the inhibitor of glycolysis and respiration is much more active than cobra venom in suppressing the synthesis of acetylcholine by the brain tissues of rats and pigeons.

TABLE III

The brain tissue was minced at about 0°, thoroughly mixed and divided into a number of approximately equal parts.

Expt.	Treatment.	Period of incubation	Total acetylcholine chloride
1.	(A) One part brain, 3·0 c c phosphate-Locke eserine (1 : 7000) solution	0 hrs.	1·50 γ/g.
	(B) Same as in (A) but glucose (0·02*M*) added to the system	2	8·45
	(C) Same as in (B) but inhibitor of respiration and glycolysis 0·06 mg. added to the system	2	5·50
	(D) Same as in (B) but cobra venom 0·2 mg. added to the system	2	4·90
2	(A) One part brain, 3·0 c·c. phosphate-Locke eserine (1 : 7000) solution and glucose (0 02*M*)	2	9·20
	(B) Same as in (A) but inhibitor of respiration and glycolysis 0·06 mg. added to the system	2	5·70
	(C) Same as in (A) but the inhibitor 0 12 mg. added to the system	2	4·75
	(D) Same as in (B) but cobra venom 0·2 mg. added to the system	2	4·60
3	(A) One part brain 3·0 c.c. phosphate-Locke eserine (1 : 7000) and glucose (0 02*M*).	2	8·88
	(B) Same as in (A) but the inhibitor 0·06 mg. added to the system	2	5·0
	(C) Same as in (A) but the inhibitor 0·12 mg. added to the system	2	4·0
	(O) Same as in (A) but cobra venom 0·2 mg. added to the system	2	4 7

CONCLUSION

The effect of cobra venom and some of the active principles isolated from it, on the synthesis of acetylcholine by the brain cells of rats and pigeons suspended in oxygenated phosphate-Locke-glucose medium has been investigated. It has been found that cobra venom inhibits the synthesis of acetylcholine and that this inhibition is very probably brought about by the inhibitor of respiration and glycolysis contained in the venom. The neurotoxin (R) which may be called the respiratory toxin, as it affects the respiratory system, has very little influence on the synthesis of the choline ester by the brain cells of rats and pigeons. It remains yet to be determined whether the observed inhibiton of respiration and glycolysis is caused by one or more than one active principle.

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PHOTOCHEMICAL FORMATION OF HYDROGEN PEROXIDE FROM WATER. PART I. IN PRESENCE OF ZINC OXIDE

By C. Narasimha Chari and M. Qureshi

The photochemical formation of hydrogen peroxide from water with zinc oxide as a sensitiser has been studied in detail both in sunlight as well as in artificial ultraviolet and visible light. The yield of hydrogen peroxide increases in presence of some organic compounds which presumably act as stabilisers. Of the nine organic substances employed for this purpose, phenol was found to be the best. An increase in the amount of zinc oxide produces a corresponding increase in the reaction rate which, however, tends to a limit with a constant intensity of light. An increase in the p_H has been found to increase the yield of hydrogen peroxide The formation of hydrogen peroxide also takes place in the total light from a tungsten filament lamp as well as in the violet region of the visible spectrum isolated by means of filters, although in the latter case the reaction is very slow. This indicates that the photosensitive range of zinc oxide extends up to the violet.

The photosensitising activity of zinc oxide, prepared by different methods, has been studied and it has been found that zinc oxide, prepared from carbonate by ignition, has the greatest activity.

The photochemical formation of hydrogen peroxide from water, photosensitised by zinc oxide, has been studied by some workers in recent years. Baur and Neuweiler (*Helv. Chim. Acta*, 1927, **10**, 901) found that exposure of aqueous suspensions of zinc oxide in contact with air to sunlight results in the formation of hydrogen peroxide. They further observed that the yield of hydrogen peroxide considerably increased in the presence of small amounts glycerol, dextrose or benzidine, the latter substances being themselves oxidised at the same time. Gopala Rao and Dhar (*vide* "Chemical Action of Light" by N. R. Dhar, 1931, p. 263) found that hydrogen peroxide was formed in relatively great quantities on the addition of very small quantities of ethylamine, methylamine, phenol, acetone, alcohol, organic acids like acetic acid and benzoic acid and inorganic substances like sodium hydroxide. Dhar and co-workers (*loc. cit.*) also observed that cadmium oxide behaves just like zinc oxide. The formation of hydrogen peroxide from water in the presence of zinc oxide was confirmed by experiments carried out by Goodeve (*Trans. Faraday Soc.*, 1937, **33**, 340). Yamafugi and Nishioeda (*Biochem. Z.*, 1938, **296**, 348; **298**, 293; 1939, **300**, 414; **303**, 260; **301**, 404; 1940, **305**, 354) observed that hydrogen peroxide was formed when aqueous solutions or suspensions of biological sensitisers, such as dried yeast extract, chlorophyll etc., were exposed to ultraviolet light, alone or in the presence of stabilisers. They believe that hydrogen peroxide is produced partly by the decomposition of water and partly by the photochemical auto-oxidation of the added substances. The object of the present investigation was to make a quantitative study of this reaction with a view to elucidating its mechanism.

Experimental

In the following work four samples of zinc oxide, prepared by different methods, have been employed. The first sample of zinc oxide was prepared by precipitating an aqueous solution of zinc nitrate while hot with a slight excess of sodium hydroxide solution. The precipitate was thoroughly washed until it was free from alkali and nitrate, dried, powdered and ignited at 800° in an electric furnace. It was then passed through 150 mesh and ignited

once again. Powdering, when necessary, was always carried out in an agate mortar. The colour of the oxide was slightly yellowish. Another sample of zinc oxide was prepared from zinc sulphate instead of zinc nitrate, by precipitation with alkali, the experimental procedure remaining the same as in the previous case. For the third sample, zinc carbonate was ignited at 400° in an electric oven for two hours. The resulting oxide was sieved and further ignited at 800°. The fourth sample of zinc oxide was prepared by igniting the nitrate at 350°. The colour of this sample was greenish yellow which persisted when the oxide was heated up to a temperature of about 1,000° for two hours in air or up to a temperature of 400° for three hours in vacuum. Morse and White (*Amer. Chem. J.*, 1892, **14**, 314) observed that oxygen and nitrous gases were tenaciously occluded by the oxide prepared by calcining the nitrate. A hot water extract of the oxide gave the test for nitrite. Small amounts of the nitrite could be leached out through repeated washing of the coloured oxide with boiling water but the colour did not altogether disappear even on prolonged washing extending over three days. All the chemicals employed in the preparation of the above samples were Merck's analytical reagents or extra-pure chemicals.

The source of illumination was a Heraeus quartz mercury vapour lamp mounted in a metallic box with a circular aperture in front and operated on 220 volt A.C. circuit in conjunction with a special transformer. The voltage between the electrodes of the mercury arc was maintained at 100 volts, the amperage being 3·5. The lamp was operated in a horizontal position parallel to the reaction vessel which was placed at a distance of 15 cm. from it The arc length was about 5 cm.

The usual method for the estimation of hydrogen peroxide employing permanganate gives inaccurate results in the presence of organic substances which are added to stabilise hydrogen peroxide. The iodometric method is more suitable for the estimation of hydrogen peroxide in the presence of organic compounds, and hence this method as modified by Kolthoff was tried by us in the present investigation. Preliminary experiments, however, revealed that this method needed further modification, with regard to the concentration of the acid used, when, as in the present case, very small amounts of hydrogen peroxide are to be estimated. A series of estimations carried out with known solutions of hydrogen peroxide of low concentrations, using the quantities of the acid and potassium iodide given by Kolthoff, indicated that more iodine was liberated than what corresponded to the amount of hydrogen peroxide in the solution, on account of the oxidation of hydriodic acid by atmospheric oxygen. The procedure, finally adopted for carrying out the estimation, was as follows:— The solution, in which hydrogen peroxide was to be estimated, was made up to 50 c.c. and to this were added 0·5 c.c. of concentrated sulphuric acid (d, 1·84), 0·2 c.c. of a N solution of ammonium molybdate and 0·3 g. of potassium iodide. The solution, after being kept in the dark for about 10 minutes, was titrated against $N/100$-sodium thiosulphate solution, using a standardised microburette, after the addition of 2 c.c. of freshly prepared starch solution. No iodine was liberated in the absence of hydrogen peroxide with the concentrations of the acid and the iodide given above within 10 minutes.

In these experiments in which the light from a quartz mercury vapour lamp or sunlight was used for irradiating the solution, care had to be taken to prevent the photolysis of hydrogen peroxide formed during the reaction. It is well known that ultraviolet rays of short wave-length (250-300 mμ) decompose solutions of hydrogen peroxide at a measurable rate. In order to prevent this simultaneous photodecomposition of hydrogen peroxide, it was

necessary to make use of a substance which would stabilise hydrogen peroxide in ultraviolet light. Anderson and Taylor (*J. Amer. Chem. Soc.*, 1923, **45**, 650, 1210) studied the inhibition of the photochemical decomposition of hydrogen peroxide solutions by various substances, both organic and inorganic, in ultraviolet light of different wave-length regions and came to the conclusion that phenol produced complete inhibition in the range $200-305\ m\mu$. Baur and Neuweiler (*loc. cit.*) noticed an increase in the yield of hydrogen peroxide when small amounts of organic substances were added to aqueous suspensions of zinc oxide, exposed to sunlight. Evidently, the increased yield is due to the inhibitory action exerted by these added substances on the photodecomposition of hydrogen peroxide formed in the reaction. In order to choose the best stabiliser for the present investigation, it was necessary to undertake a comparative study of the influence of the various organic substances, which have already been found to inhibit the thermal and photodecomposition of hydrogen peroxide. For this purpose, aqueous suspensions of zinc oxide, each containing 0·2 g. of the oxide in 30 c.c. of twice distilled conductivity water and an exact quantity of a stabiliser, sufficient to make the solution 0·1*M* with respect to it, were exposed in open pyrex flasks to sunlight. After a period of five hours all the flasks were removed at the same time. The contents of the flasks were filtered, the precipitates washed well and the hydrogen peroxide content of each was estimated according to the procedure already described. The results are shown in the following table in which *C* represents the amount of hydrogen peroxide formed in g. moles per litre.

TABLE I

Zinc oxide (c. p. Merck, 0·2 g.), conductivity water (30 c. c.), and stabiliser (0·1*M*) exposed to sunlight for 5 hours.

Stabiliser ...	Phenol	Glycerol	Acetanilide	EtOH	Et_2O	Acetone	Benzidine	Salicylic acid	Oxalic acid
$C \times 10^6$ ...	57·30	44·30	42·85	30·60	19·55	14·60	6·45	4·45	0·55

It is evident from the above that phenol exerts the greatest stabilising effect on the reaction. The other substances are given in the decreaing order of efficiency. These results have been confirmed by repeating the experiments several times.

In the experiments described below phenol or glycerol was used as a stabiliser, the quantity used being such that the solution was always 0·1*M* with respect to it.

Effect of varying the amount of the Photosensitiser.—In these experiments, 30 c.c. of conductivity water containing varying amounts of zinc oxide (prepared from nitrate by precipitation) and a fixed amount of phenol were exposed to the total ultraviolet light from a mercury vapour lamp in a quartz flask for two hours.

TABLE II

Zinc oxide, conductivity water (30 c.c.) and phenol (0·1*M*) exposed to total ultraviolet light for 2 hours.

Zinc oxide (g.)	0·01	0·03	0·05	0·10	0·20
$C \times 10^6$	0·38	0·79	1·07	1·10	1·10

The results, given above, indicate an increase in the amount of hydrogen peroxide with a corresponding increase in the quantity of the photosensitiser.

Influence of Time of Exposure.—In these experiments an aqueous suspension of zinc oxide containing phenol as a stabiliser was exposed for different periods of time to the light from a quartz mercury vapour lamp focussed by a glass condenser. The reaction vessel was a rectangular glass cell of 25 c.c. capacity with a tubular opening. The results are given in the following table.

TABLE III

Zinc oxide (prepared from nitrate, 0·1 g.), conductivity water (15 c.c.) and phenol (0·1*M*) exposed to light from a quartz mercury vapour lamp.

Time of exposure (hrs.) ...	2	4	6	8	10	12
$C \times 10^6$	0·60	0·95	1·25	1·40	2·10	2·30

Experiments in Monochromatic light in the Visible Region.—The photochemical formation of hydrogen peroxide from water takes place in the presence of zinc oxide in sunlight. As sunlight also includes ultraviolet rays which are transmitted by glass, it was of interest to find out if zinc oxide is capable of bringing about this reaction in the visible light from which ultraviolet rays have been completely eliminated and if so which part of the visible light is concerned in this process. For this purpose experiments were carried out with monochromatic visible light, isolated by means of Wratten gelatine-glass filters. The source of light was a quartz mercury vapour lamp. Exposure to violet light (400—470 mμ), for ten hours produced about $0{\cdot}25 \times 10^{-6}$ g. moles per litre of hydrogen peroxide, while in other parts of the visible spectrum, hydrogen peroxide could not be detected. This shows that the photosensitive range of zinc oxide extends up to 435 mμ.

Effect of p_H.—In these experiments, the source of visible light was a 1000 watt tungsten filament lamp connected to 220 A.C. mains in series with a resistance and an ammeter and enclosed in a wooden box having a circular aperture in front. A high degree of intensity was secured by the use of a reflector. The reaction vessel which was a flat-bottomed pyrex flask of 50 c.c. capacity was placed at a distance of 37 cm. from the source of light. The heat rays were cut off by a hollow glass filter through which water was circulated. The light was brought to focus inside the reaction vessel by means of a glass condenser. The results of this experiment are summarised in the following table.

TABLE IV

ZnO (prepared from sulphate, 0·2 g.), aqueous solution of NaOH (30 c.c.) and glycerol exposed to light from a 1000 watt lamp for 5 hours.

NaOH (moles/litre) ...	Nil	0·005	0·01	0·017	0·05	0·083	0·167	0·33	0·50
$C \times 10^6$	0·20	0·85	0·95	1·15	1·70	2·35	2·45	2·55	3·50

The above results indicate that in alkaline solution, the yield of hydrogen peroxide increases with an increase in p_H value.

Sensitising Action of different samples of Zinc Oxide.—The following experiments were performed to compare the sensitising activity of zinc oxide prepared by the different methods mentioned above. The results are summarised in Tables VI-IX. In these tables the letters C. I. indicate the sample prepared from carbonate by ignition, S. P., the sample prepared from sulphate by precipitation, N. P., the sample prepared from nitrate by precipitation and N. I., the sample prepared from nitrate by ignition.

TABLE VI

Zinc oxide (0·1 g.), conductivity water (15 c.c.) and phenol (0·1M) exposed to light from a quartz mercury vapour lamp focussed by a glass condenser for 2 hours.

ZnO	(C. I.)	(S. P)	(N. P.)	(N. I.)
$C \times 10^6$	1·25	0·80	0·75	Traces

TABLE VII

Zinc oxide (0·2 g.), conductivity water (30 c.c.), and phenol (0·1M) exposed to light from 1000 watt lamp for 5 hours.

ZnO	(C. I.)	(S. P.)	(N. P.)	(N. I.)
$C \times 10^6$	0·75	0·70	0·50	Traces

TABLE VIII

Zinc oxide (0·2 g), conductivity water (30 c.c.) and phenol (0·1M) exposed in open pyrex flasks to sunlight for 5 hours.

ZnO	(C. I.)	(S. P.)	(N. P.)	(N. I.)	(S.P.B.)
$C \times 10^6$	32·0	26·35	20·05	2·85	0·75

In the above table the letters (S. P. B) indicate the sample prepared from sulphate by precipitation. An aqueous suspension of this sample was exposed in the absence of phenol and as such serves as a blank.

TABLE IX

ZnO (0·2 g.), conductivity water (30 c.c.), and glycerol (0·1M) exposed in open pyrex flasks to sunlight for 5 hours.

ZnO	(C.I.)	(S.P.)	(N.P.)	(N.I.)
$C \times 10^6$	17·60	10·55	2·5	1·35

These results indicate that zinc oxide prepared from carbonate by ignition has the greatest activity, while the oxide prepared from the nitrate by ignition is the least active. The activities of the other two samples lie between these two extremes. The relatively low activity of the sample prepared from nitrate by ignition is probably due to the presence of adsorbed oxides of nitrogen which lends colour to the sample. This point will be referred to in the discussion.

DISCUSSION

The photochemical formation of hydrogen peroxide from water in contact with air takes place in sunlight as well as in artificial ultraviolet and visible light in the presence of zinc oxide.

The yield of hydrogen peroxide increases in the presence of some organic compounds such as phenol, glycerol, acetanilide, ethyl alcohol, ether, acetone, benzidine, salicylic acid and oxalic acid. No hydrogen peroxide was, however, detected when aqueous solutions of these substances were exposed to light in blank experiments in the absence of zinc oxide, which shows that these substances either take an active part in the process of the formation of hydrogen peroxide through zinc oxide or they simply help in stabilising hydrogen peroxide formed in the process, or act in both ways. The part played by these substance in the reaction will be discussed in a subsequent communication.

From a study of the photosensitisation by zinc oxide in monochromatic light, secured by means of light filters, it was found that some hydrogen peroxide was also formed in the

violet region of the visible spectrum (400-470 mμ). This indicates that the photosensitive range of zinc oxide extends up to the violet. Goodeve (*loc. cit.*) from a study of the diffuse reflection spectra of zinc oxide determined the position of its absorption band. There was a sharp fall in the reflecting power of the powder at 385 mμ, indicating the entry of a strong absorption band with a fairly sharp threshold at the wave-length. Hence it was concluded that zinc oxide absorbs in the near ultraviolet, which is exactly the region in which the oxide is found to be photo-active. But our results show that the photo-active range of zinc oxide and consequently its absorption extends even up to the violet *i.e.*, 435 mμ.

Of all the four samples of zinc oxide tried, the one prepared from carbonate by ignition was found to possess the greatest activity. Richards and Rogers (*Amer. Chem. J.*, 1893, **15**, 567) have shown that zinc oxide prepared by the ignition of the carbonate always carries occluded gases which mainly consist of carbon dioxide and oxygen. It is also well known that zinc oxide adsorbs carbon dioxide from the air. These observations led the present authors to the idea that zinc carbonate itself might also sensitise the reaction. Preliminary experiments tried with zinc carbonate powder confirmed the idea. Detailed quantitative study of zinc carbonate as a sensitiser in this reaction will form the subject matter of a later paper.

Zinc oxide prepared from nitrate by ignition was found to be the least active of all the samples tried. The greenish yellow colour of the sample has been shown to be due to the occlusion of oxides of nitrogen. The lower yield of hydrogen peroxide with the sample might be explained as being due to the partial destruction of hydrogen peroxide formed during the reaction by the nitrite present in the system.

Further work directed towards the elucidation of the mechanism of this reaction is in progress.

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SUPERSATURATION LIMITS OF SOLUTIONS. PART II

By Rama Gopal

In continuation with the previous work a few more salts have been studied. The results obtained appear to show that $\lambda (T_s - T)$ is, in general, proportional to σV_M, the terms used have their usual significance. In particular cases where σV_M values are not very different, $\lambda (T_s - T)$ is approximately a constant.

A new method for calculating the radius r, of the stable crystal nucleus at the first temperature of spontaneous crystallisation under specified conditions, has been developed and it is shown that r is of the order of 10^{-6}cm. Further r is found to vary hyperbolically with the degree of supersaturation.

The limits of supersaturation $T_s - T$ for halides and nitrates of K, Rb, and Cs have been calculated from the formula $T_s - T = 13\sigma V_M/\lambda$ and it is pointed out that the results obtained are similar to the conclusion arrived at by Jones.

In a previous communication (*J. Indian Chem. Soc.*, 1943, **20**, 183) it has been shown that $\lambda (T_s - T)$, where T_s denotes the saturation temperature, T, the temperature of first spontaneous crystallisation and λ, the heat of solution, is nearly a constant in the case of a number of monovalent salts of sodium and potassium and that its value is approximately 80,000 cals. under conditions specified in the communication. This work has been extended and a number of other substances have been investigated. Experimental arrangements are the same as before and the results obtained are given in Table I.

Table I

K_2SO_4

T_s.	T.	$T_s - T$.
48	20·4, — , —	27·6
50	25·0,26·8,26·0	25·0
55	29·4,28·2,28·0	24·6
58	30·2, — , —	27·8
60	32·8,32·4,32·6	27·2
63	36·0,36·2,35·8	27·0
65	37·6,38·0,36·8	27·4
70	43·0,42·8,42·0	27·0

Approx. mean = 27·0

$K_2Cr_2O_7$

T_s.	T.	$T_s - T$.
40	27·0,25·2,23·0	13·0
45	32·2,30·0,30·0*	12·8
50	36·8,36·4,32·4	13·2
55	41·6,40·2,31·0	13·4
60	46·4,43·2,40·2	13·6
65	52·4,50·4,35·8	12·6
70	56·2,54·2,46·2	13·8
75	62·0,59·2,52·4	13·0

Approx. mean = 13·2

$K_3Fe(CN)_6$

T_s.	T.	$T_s - T$.
35	24·0,23·2,20·0*	11·0
40	28·2,25·0,27·6	11·8
45	32·6,33·6,32·0	12·4
50	37·4,36·2,37·0	12·6
55	43·4,42·0,41·6	12·6
60	47·8,48·4,48·0	12·2
65	52·0,51·4,45·2	12·6

Approx. mean = 12·0

$K_4Fe(CN)_6$

T_s.	T.	$T_s - T$.
50	25·2,22·0,23·8	24·8(?)
55	30·0,26·4,21·0*	25·0(?)
60	37·8,35·0,32·8	22·8(?)
65	46·0,40·2,39·0	19·0
70	51·4,52·4,42·8	18·6
75	55·4,53·2,49·6	19·6
80	62·0,58·4,50·4	18·0

Approx mean = 18·4

K_2CrO_4 **

T_s.	T.	$T_s - T$.
70	36·2	33·8
65	32·4	32·6
60	27·0	33·0
		33·0

$HgCl_2$

T_s.	T.	$T_s - T$
50	26·8, — , —	23·2
55	31·2,31·0,25·0	23·8
60	35·2,34·0,34·2	24·8
65	41·0,39·8,40·4	24·0
70	43·0,35·0, —	27·0
80	54·0,53·8,53·8	26·0

Approx. mean = 25·0

$Ba(NO_3)_2$

$T_s - T$ is about 18·5° (*vide* previous paper)

* Solutions did not crystallise down to these temperatures.

** Dissolution of the substance is extremely slow and hence this operation takes a very long time. Consequently the data are not very reliable as the continuous heating might vitiate the limits. Besides the slow dissolution makes a more detailed investigation of the substance almost impossible.

Evidently from Table I, $T_s - T$ is almost a constant for the same substance irrespective of the value of T_s provided T is taken as the temperature of first spontaneous crystallisation. On subsequent heatings to redissolve the crystals, it is found that, in general, T goes on decreasing thereby $T_s - T$ is increased. This phenomenon is a very general one and will receive full attention in a separate communication. The values of λ $(T_s - T)$ vary considerably from substance to substance as is clear from Table II.

TABLE II

Salt.	$-\lambda$ in cals.	$T_s - T$	λ^* $(T_s - T)$.
$HgCl_2$	3300	25 0	82500
K_2SO_4	6380	27·0	176860
K_2CrO_4	5230	33·0	172790
$Ba(NO_3)_2$	9400	18 5	173900
$K_3Fe(CN)_6$	14400	12 0	172800
$K_2Cr_2O_7$	16700	13 5	225450
$K_4Fe(CN)_6$	16900	20 0	338000

TABLE III

Salt.	λ $(T_s - T)$.	$^{**}\sigma V_M$.	$\frac{\lambda\ (T_s - T)}{\sigma V_M}$
KCl	78897	5693	13·9
KBr	82804	6019	13 7
KI	79205	6707	11·9
KNO_3	114400	6555	17·4 (?)
$NaNO_3$	65390	4813	13·6
NaCl	62220	4449	13·9
K_2SO_4	171860	14040	12·3
$K_2Cr_2O_7$	225450	19166	11·8

The significance of the variation in the value of λ $(T_s - T)$ is discussed below.

Relation between λ $(T_s - T)$ and σ V_M.—In the derivation of the relationship

$$\lambda\ (T_s - T) = 2\sigma V_M \times \frac{T_s}{r}\ ,$$

it was assumed that if T_s in the case of similar substances were almost a constant, then $\lambda(T_s - T)$ should vary directly as σV_M. As the values of σ for all the substances investigated are not known, it is not possible to verify the generality of the latter statement; but from the scanty figures which are available it may be concluded that surface energy and molecular volume, most probably, play a very important rôle in the spontaneous crystallisation of these substances (*vide* Table III).

The last column of Table III shows clearly that $\lambda(T_s - T)$ is approximately proportional to the product σV_M. Hence it appears to be fairly justified to assume that the factor T_s/r is approximately constant for substances mentioned in Table III. In other words, the spontaneous crystallisation of the aqueous solutions of any of these salts depends to a great extent on its heat of solution λ, its specific surface energy, σ and its molecular volume V_M under identical conditions. In short the experimental results obtained hitherto lead to the following conclusions :—

(1) λ $(T_s - T)$ is, in general, proportional to σV_M.

(2) For substances whose σV_M values are approximately equal, the limit of supersaturation $T_s - T$ varies inversely as the molecular heat of solution λ.

A New Method for Calculating the Value of r, the Radius of the Stable Crystal Nucleus at the Temperature of its Spontaneous Crystallisation.—Making use of the relationship $\frac{\lambda(T_s - T)}{\sigma V_M} = 13{\cdot}0$, an estimate of the size of the stable crystal nucleus can be made with the help of the equation $\lambda(T_s - T) = 2\sigma V_M\ T_s/r$ in the following way :—

* Only positive numerical value of λ should be considered (see author's previous communication).

** The value of σ used is of the melt of the substance concerned and is the intrapolated (to 30°) value from the experimental data supplied by Jaeger (*Z. anorg. Chem.*, 1917, **101**, 185).

$$\therefore \lambda(T_S - T)J = 2\sigma V_M T_S / r \text{ (}\lambda\text{ converted into ergs).}$$

or

$$r = \frac{2\sigma V_M}{\lambda(T_S - T)J} T_S \qquad \dots \quad (1)$$

Substituting 13·0 for $\frac{\lambda(T_S - T)}{\sigma V_M}$ in (1) we get,

$$r = \frac{2}{13 \times 4{\cdot}2 \times 10^7} T_S = 0{\cdot}036 \times 10^{-7} T_S \text{ cm.} \qquad \dots \quad (2)$$

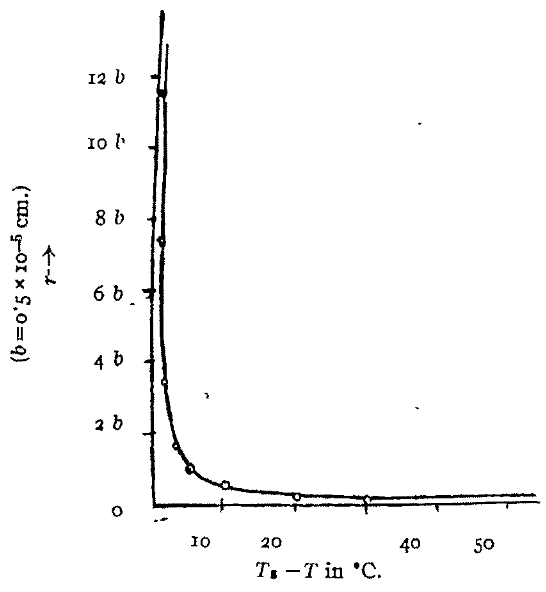
From this equation the values of r for different values of T_S have been calculated and are given in Table IV.

TABLE IV

T_S in °C	...	10°	20°	30°	40°	50°
$r \times 10^6$ cm.	...	1·0	1·03	1·08	1·10	1·13

From Table IV it appears that the size of the stable crystal nucleus is about 100 times the molecular dimensions. Ostwald considered that the particles containing less than 10^8 to 10^{12} atoms or molecules are incapable of inducing crystallisation in supersaturated solutions. Assuming the crystal nucleus to be spherical, its radius in aqueous solutions of KCl at the lower limit considered by Ostwald amounts to $1{\cdot}2 \times 10^{-5}$ cm. and $2{\cdot}5 \times 10^{-4}$ cm. respectively which is 10 to 100 times as large as those given above. However, the values obtained in this paper are supported by the researches of a number of workers. McIntosh (*Trans. Roy. Soc. Canada*, 1819, **13**, *iii*, 265) has shown that in salol the necessary mass to cause crystallisation does not exceed 4×10^{-15} g., which gives a particle of radius less 1×10^{-5} cm. Tammann and Gronow (*Z. anorg. Chem.*, 1931, **200**, 57) consider that the active particle is generally of a size containing atoms and molecules 10^7 times less than that suggested by Ostwald. Hence radii of such particles at the two limits considered by Ostwald are $1{\cdot}2 \times 10^{-6}$ cm. and $5{\cdot}5 \times 10^{-8}$ cm., the former of which agrees with the results obtained here. Hamburger (*Chem. Weekblad.*, 1938, **35**, 886) considered the size of the active nucleus for high supersaturation of poorly soluble substances to be made of only a few atoms and molecules specially under the influence of the absorptive forces of the walls of the container. On the other hand Hinshelwood and Hartley (*Phil. Mag.*, 1922, **43**, 78) have calculated the radius of the stable crystal nucleus for a few organic melts by the application of the Nernst Heat Theorem (a modification of the Ostwald's method). The value obtained by them for undercooled p-toluidine melt is of the order of 10^{-5} cm. when the value of σ used is 10^3 ergs. per sq. cm. It appears that

FIG. 1



the value of σ used is too high. According to Jaeger (*loc. cit.*) σ for *o*-toluidine is about 40 ergs per sq. cm. at 25°. There is no reason to suppose that it will rise to 1000 ergs in its *para*-form. Hence taking σ for *o*-toluidine to be about 50 ergs (its density being a little higher than the *o*-form its σ should be a little greater) the radius becomes about $1{\cdot}1 \times 10^{-6}$ cm. at 25°, a value quite in agreement with that obtained in this investigation. It appears therefore to be fairly certain that the radius of the active crystal nucleus is of the order of 10^{-6} cm. The nucleus of a radius 10^{-5} cm. appears to be too large and it will act as an active centre even in the immediate neighbourhood of the saturation temperature as will be clear from Fig. 1.

Some General Results on Supersaturation

The results arrived at thus far lead to the following important conclusions :—

The radius r of the stable crystal nucleus at any temperature T, in an aqueous solution saturated at T_s is, in general, given by the expression

$$r = 2\sigma V_M T_s / \lambda (T_s - T) J \qquad \ldots \quad (3)$$

For a number of substances $\dfrac{\lambda(T_s - T)}{\sigma V_M}$ values are approximately equal under specified conditions (Table IV), hence r is proportional to T_s in these cases. The value of r under these conditions is of the order of 10^{-6} cm. Further from (3) it is clear that r is proportional to $T_s/(T_s - T)$ for any particular solute as now σ, V_M and λ are constants. Consequently different solutions (T_s varies) of the same substance will have different values of r at the same temperature (T is kept constant).

Equation (3) can be written as

$$r\,(T_s - T) = 2\,\sigma V_M\, T_s/\lambda\, J \qquad \ldots \quad (4)$$

If for any particular solute T_s is kept constant (4) reduces to

$$r\,(T_s - T) = \text{a constant.} \qquad \ldots \quad (5)$$

The equation (5) shows that r varies hyperbolically with the degree of supersaturation $T_s - T$. For a solution of KCl saturated at $T_s = 300°$K (5) becomes

$$r(T_s - T) = 2 \times 5693 \times 300/4046 \times 4{\cdot}2 \times 10^7 = 1{\cdot}8 \times 10^{-5} \qquad \ldots \quad (6)$$

Plotting r against $T_s - T$ a rectangular hyperbola is obtained as shown in Fig. 1.

It is clear that in the begining, inspite of large reduction in the value of r from $r = \infty$ to $r = 10^{-5}$ cm., the degree of supersaturation is so small that the formation of an active crystal nucleus is very improbable. However, the curve takes a very sharp bend in the neighbourhood of $r = 10^{-6}$ cm. and now $T_s - T$ rapidly increases with slight variations in r. Hence formation of stable crystal nucleus leading to spontaneous crystallisation is very probable within this region. The curve gives a satisfactory explanation of the hyperbolic nature of the energy—$(T_s - T)$ diagrams obtained by Young and others (*J. Amer. Chem. Soc.*, 1911, **33**, 158) in a number of cases. A very large value of r in the immediate neighbourhood of T_s requires an impact of large energy content for the formation of the stable crystal nucleus which may start crystallisation whereas reverse will be the case when the degree of supersaturation is very large.

The relationship $\lambda(T_s - T) =$ a constant has been employed with success in supersaturated solutions of $KClO_4$ whose data for $T_s - T$ under given conditions have already been published (*loc. cit.*). Considering $KClO_4$ to belong to the category of other monovalent salts of potassium its limit of supersaturation $T_s - T$ should be about 80000/12100 or 6·6 degrees. Some experiments with sealed solutions of $KClO_4$ were performed using solubilities given in Comey and Hahns' "Dictionary of Solubilities etc." The temperature of spontaneous crystallisation appeared to be indefinite and $T_s - T$ was always less than 4°. It was therefore suspected that the solubility data given in this book might be erroneous. Bornstein Tables (recent editions) were then consulted and it was found that recently determined solubilities were quite different from the older values. Experiment with these solubility figures yielded results quite in agreement with the expected value of $T_s - T$ for $KClO_4$.

With this successful application and utility of the result $\lambda(T_s - T) =$ a constant a little hypothetical indulgence may be permitted. For any theoretical prediction, one may consider solutions with relatively smaller viscosities and therefore a free movement of the crystal forming units is possible in these solutions. For highly viscous solutions nothing can be foretold as the formation of the crystal nuclei is very uncertain and improbable, and their growth is very slow due to hindrance in the free movement of the units. Again the rate of cooling of the solution should be neither too rapid nor too slow. The former does not give time enough for the crystal nucleus to grow and further at a lower temperature which is quickly attained increase in viscosity and decrease in molecular motion (*cf.* Freundlich, "Colloid and Capillary Chemistry", 1922, p. 319) hinder the formation of the crystal nucleus, while the latter condition gives too much time, and, probablity for crystalline nucleus to be formed above the normal value of T is very great and this will naturally favour a lower supersaturation than predicted by the above relationship. As the aqueous solutions of the salts of K, Rb and Cs of the common inorganic acids will be very suitable for treatment in this manner, these will be considered here, Here again it is assumed that T_s/τ is approximately the same in all these cases and hence $T_s - T = 13\,\sigma V_M/\lambda$.

Table V gives the values of supersaturation limits $T_s - T$ for aqueous solutions of halides and nitrates of K, Rb and Cs calculated from the above formula. Experimental values for K salts are given in a previous communication (*loc. cit.*). In these calculations the values of λ at high dilutions and specific surface energy values σ intrapolated to 30° from the experimental data of Jaeger for melts of these sucstances, have been employed in all these cases. Naturally much reliance and accuracy should not be expected and values must be treated as highly approximate figures. Nevertheless they give an idea of the extent of supersaturation obtainable in these solutions.

TABLE V

Supersaturation limits of some aqueous solutions calculated from the formula

$$T_s - T = 13\,\sigma V_M/\lambda$$

Cation	Anion: Cl^-				Br^-				I^-				NO_3^-			
	λ	σ	σV_M	$T_s - T$	λ	σ	σV_M	$T_s - T$	λ	σ	σV_M	$T_s - T$	λ	σ	σV_M	$T_s - T$
K^+	4046	151	5693	18·3*	5080	139	6019	15·4*	5110	127	6707	16·9*	8520	136	6550	9·6*
Rb^+	4500	146	6132	17·8	5960	138	6979	15·2	6500	126	7862	15·6	—	129	8515	—
Cs^+	4750	136	5712	15·6	6300	128	6144	12·6	8104	106	6116	9·6	—	120	6240	—

* Experimental values in the above order are 19·5, 16·3, 15·5 and 13·0.

It appears from Table V that $T_s - T$, in general, is in a decreasing order of K, Rb and Cs. This is in agreement with the conclusion arrived at by Jones (*J. Chem. Soc.*, 1908, **93**, 1739), who found that the degrees of supersaturations of KNO_3, $Rb NO_3$ and $CsNO_3$, in equally rocked solutions are 4°, 1° and 0° respectively. Unfortunately the lack of data for λ of these salts does not permit verification of these results but from an analogy with the halides of these metals the results appear to be in general agreement. Further, the degrees of supersaturation vary roughly as the inverse of the respective molecular weight, a conclusion arrived at by Jones.

The values of the limits of supersaturation given in Table V for Rb and Cs salts may be a little too high. A lower hydration and higher ionic volume of these ions as compared with that of K^+ may favour a lower supersaturation as both these properties offer better chances of forming stable crystal nuclei at lower degrees of supersaturation. Further the salts may be expected to have an almost constant $T_s - T$, *i.e.*, it is almost independent of the amount of heating as in the case of many K salts.

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SYNTHESIS OF COUMARINS FROM O-HYDROXYBENZOPHENONES

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5-Methyl-, 5-chloro-, 3-chloro-5-methyl-2-methoxybenzophenones have been condensed with ethyl bromoacetate and ethyl α-bromopropionate under Reformatsky's condition to yield hydroxy esters which have been dehydrated to the unsaturated esters and the latter on demethylation give quantitative yields of coumarin derivatives.

In continuation of the work of Chakravarti *et al* (Chakravarti and Mazumdar, *J. Indian Chem. Soc*, 1938, **15**, 136; Chakravarti and Dutta, *ibid.*, 1940, **17**, 65; Chakravarti and Bera, *ibid.*, 1944, **21**, 44) on the synthesis of coumarin derivatives from *o*-hydroxy-aryl-alkyl ketones it has been found that the *o*-hydroxybenzophenones also give good yields of coumarin derivatives.

The ketones *e.g.*, 2-methoxy-5-methyl-, 2-methoxy-5-chloro- and 2-methoxy-3-chloro-5-methyl-benzophenones have been condensed with ethyl bromoacetate and with ethyl α-bromopropionate forming hydroxy-esters, which have been treated with thionyl chloride and pyridine to yield unsaturated esters. These unsaturated esters on being treated with hydriodic acid yield coumarins quantitatively.

Ketones used.	Halogenated fatty ester	Coumarins obtained.
2-Methoxy-5-methylbenzophenone	Ethyl bromoacetate	4-Phenyl-6-methylcoumarin
2-Methoxy-5-chlorobenzophenone	Ethyl bromoacetate	4-Phenyl-6-chlorocoumarin
,,	Ethyl α-bromopropionate	3-Methyl-4-phenyl-6-chlorocoumarin
2-Methoxy-3-chloro-5-methylbenzophenone	Ethyl bromoacetate	4-Phenyl-6-methyl-8-chlorocoumarin
,,	Ethyl α-bromopropionate	3:6-Dimethyl-4 phenyl 8-chlorocoumarin

Experimental

Preparation of 4-Phenyl-6-methylcoumarin from 2-Hydroxy-5-methylbenzophenone

2-Hydroxy-5-methylbenzophenone.—The benzoate of *p*-cresol (26 g.) was mixed with finely powdered anhydrous aluminium chloride (30 g.) and the mixture heated at 130-40° in the absence of moisture for 1 hour. The glassy mass was decomposed with ice-cold dilute hydrochloric acid, when the product solidified and it was crystallised from dilute alcohol as yellow needles, m p. 87°, yield 23 g. It is identical with the compound prepared by Rosenmünd and Schnürr (*Annalen,* 1927, **460**, 84). *2-Methoxy-5-methylbenzophenone* was obtained by the methylation of the above compound with dimethyl sulphate in the usual manner. The oil obtained was taken up with ether, the ethereal extract washed with water and dried over anhydrous sodium sulphate. It distilled at 190°/4 mm. as a yellow oil. (Found: C, 79.58; H, 6.20. $C_{15}H_{14}O_2$ requires C, 79.65; H, 6.19 per cent).

4-Phenyl-6-methylcoumarin.—*Ethyl 2-methoxy-5-methyl-β-phenylcinnamate,* prepared by the reaction of 2-methoxy-5-methylbenzophenone and ethyl bromoacetate in the presence of zinc wool and the subsequent dehydration of the hydroxy-ester with thionyl chloride and pyridine in the usual manner, distilled at 199-200°/4.5 mm. as a brown oil. (Found: C,

76·98 ; H, 6·76. $C_{19}H_{20}O_3$ requires C, 77·03 ; H, 6·76 per cent). The unsaturated ester on demethylation with hydriodic acid (sp. gr. 1·7) gave 4-phenyl-6-methylcoumarin, which crystallised from dilute alcohol as colourless shining needles, m.p. 131°. (Found : C, 81·43 ; H, 5·10. $C_{16}H_{12}O_2$ requires C, 81·36 ; H' 5·09 per cent).

Preparation of 4-Phenyl-6-chlorocoumarin and 3-Methyl-4-phenyl-6-chlorocoumarin from 2-Hydroxy-5-chlorobenzophenone

2-Hydroxy-5-chlorobenzophenone.—The benzoate of *p*-chlorophenol (25 g.) was mixed with anhydrous aluminium chloride (26 g.) and the mixture heated in the absence of moisture at 130-40° for 1 hour. The mixture was treated with ice-cold dilute hydrochloric acid, when the product solidfied on cooling. It was crystallised from dilute alcohol as yellow needles, m.p. 96-97°, yield 18 g. (Found : Cl, 15·54. $C_{13}H_9O_2$ Cl requires Cl, 15·27 per cent).

2-Methoxy-5-chlorobenzophenone was prepared from 2-hydroxy-5-chlorobenzophenone with dimethyl sulphate as usual. It was crystallised from dilute alcohol as colourless needles, m.p. 103-104°. (Found . Cl, 14·44. $C_{14}H_{11}O_2$ Cl requires Cl, 14·40 per cent).

4-Phenyl-6-chlorocoumarin.—*Ethyl 2-methoxy 5-chloro-β-phenylcinnamate* was prepared by the condensation of 2-methoxy-5-chlorobenzophenone with ethyl bromoacetate using zinc wool and the hydroxy-ester was dehydrated with thionyl chloride in the presence of pyridine. It distilled at 216°/2 mm. as a brown oil. (Found : Cl, 11·19. $C_{18}H_{17}O_3Cl$ requires Cl, 11·22 per cent). 4-Phenyl-6-chlorocoumarin was obtained by the demethylation of the above unsaturated ester with hydriodic acid. It crystallised from dilute alcohol as colourless needles, m.p. 156°. (Found : Cl, 13·79. $C_{15}H_9O_2Cl$ requires Cl, 13·84 per cent).

3-Methyl-4-phenyl-6-chlorocoumarin.—*Ethyl 2-methoxy-5-chloro-α-methyl-β-phenylcinnamate* was prepared by the condensation of 2-methoxy-5-chlorobenzophenone with ethyl α-bromopropionate in the presence of zinc wool and the subsequent dehydration of the hydroxy-ester with thionyl chloride and pyridine. It distilled at 206°/2 mm. as a brown oil. (Found : Cl, 10·69. $C_{19}H_{19}O_3$ Cl requires Cl, 10·74 per cent). On demethylation with hydriodic acid this unsaturated ester gave 3-methyl-4-phenyl-6-chlorocoumarin, which crystallised from dilute alcohol as needles, m.p. 124°. (Found : Cl, 13·11. $C_{16}H_{11}O_2Cl$ requires Cl, 13·12 per cent).

Preparation of 4-Phenyl-6-methyl-8-chlorocoumarin and and 3 : 6-Dimethyl-4-phenyl-8-chlorocoumarin from 2-Hydroxy-3-chloro-5-methyl-benzophenone

2-Hydroxy-3-chloro-5-methyl-benzophenone.—It was prepared from the benzoate of 2-chloro-4-methylphenol (30 g.) and anhydrous aluminium chloride (30 g.) by heating at 120-30° for 1 hour. The cooled mass was acidified with dilute hydrochloric acid, extracted with ether, the ethereal solution washed with dilute alkali solution then with water and finally dried over anhydrous sodium sulphate. On removal of ether the residue was distilled at 220°/6·5 mm. as a yellow liquid, which solidified to yellow needles, m.p. 81°, yield 20 g. (Found : Cl, 14·22. $C_{14}H_{11}O_2$ Cl requires Cl, 14·40 per cent).

2-Methoxy-3-chloro-5-methyl-benzophenone was obtained from 2-hydroxy-3-chloro-5-methyl-benzophenone by the action of dimethyl sulphate in the usual manner. It distilled at 190°/2 mm. as a thick yellow oil. (Found : Cl, 13·46. $C_{15}H_{13}O_2$ Cl, requires Cl, 13·63 per cent).

4-Phenyl-6-methyl-8-chlorocoumarin.—*Ethyl 2-methoxy-3-chloro-5-methyl-β-phenyl cinnamate* was obtained by the condensation of 2-methoxy-3-chloro-5-methylbenzophenone and ethyl bromoacetate using zinc wool and the subsequent dehydration of the hydroxy-ester with thionyl chloride and pyridine in the usual manner. It distilled at 215°/2 mm. as a brown viscous oil. (Found: Cl, 10·70. $C_{19}H_{19}O_3Cl$ requires Cl, 10·74 per cent). This unsaturated ester on demethylation with hydriodic acid gave 4-phenyl-6-methyl-8-chlorocoumarin, which crystallised from dilute alcohol as colourless light needles, m.p. 152-53°. (Found: Cl, 13·15. $C_{16}H_{11}O_2$ Cl requires Cl, 13·12 per cent).

3 : 6-Dimethyl-4-phenyl-8-chlorocoumarin.—*Ethyl 2-methoxy-3-chloro-α : 5-dimethyl-β-phenylcinnamate* was prepared by the reaction of 2-methoxy-3-chloro-5-methylbenzophenone with ethyl α-bromo-propionate in the presence of zinc wool and the hydroxy-ester was dehydrated with thionyl chloride and pyridine. It crystallised from ether as colourless needles, m.p. 120°. (Found: Cl, 10·33. $C_{20}H_{21}O_3Cl$ requires Cl, 10·30 per cent). The unsaturated ester was demethylated with hydriodic acid to give 3 : 6-dimethyl-4-phenyl-8-chlorocoumarin. It crystallised from dilute alcohol as colourless needles, m.p. 172°. (Found: Cl, 12·42. $C_{17}H_{13}O_2$ Cl requires Cl, 12·48 per cent).

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HALOGENATION. PART XXIII. HALOGENATION OF FLUOROBENZENE, *o*-, *m*-, AND *p*-FLUOROTOLUENES

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Fluorobenzene, *o*-, *m*- and *p*-fluorotoluenes have been chlorinated, brominated and iodinated under different conditions as a result of which mixed halogen derivatives have been obtained by direct halogenation.

The majority of the mixed halogen derivatives of fluorobenzene have been generally obtained either from fluoroanilines or other halogenated anilines, through the Sandmeyer's reaction. By passing chlorine into flurobenzene in presence of iron, Wallach and Hensler (*Annalen*, 1905, **248**, 225) obtained *p*- fluorochlorobenzene and a dichloro product, considered to be either 2:4- or 3:4-dichlorofluorobenzene or a mixture of both, as separation is not possible due to the close boiling point (Van De Laude, *Rec. trav. chim.*, 1932, **51**, 98; Kraay, *ibid.*, 1929, **48**, 1055). By a similar method Wallach and Hensler (*loc. cit.*) obtained *p*-bromofluorobenzene and two isomeric dibromofluorobenzenes, one a liquid boiling at 109-12°/30 mm. and a solid, m.p. 69°, which is also obtained during the bromination of fluorobenzene (Schieman and Pelarsky, *Ber.*, 1931, **64B**, 1340) and described as 2:4- or 3:4-dibromofluorobenzene. The liquid dibromo product has been obtained from 2:4-dibromoaniline, through the diazonium fluoroborate and hence, the solid product is obviously 3:4-dibromofluorobenzene.

Very little work has been done on the halogen derivatives of *o*-, *m*- and *p*-fluorotoluenes. By the direct action of chlorine, bromine and iodine in presence of catalyst, many mixed halogen derivatives have now been prepared. The constitution of the compounds, so prepared, has been determined in as many cases as possible either by referring them to compounds already known or by oxidising them to known derivatives of fluorobenzoic acids, or synthesising them from the corresponding amino compounds by replacing the amino group by Sandmeyer's reaction by the suitable halogen atom. In a few cases the position of the entering halogen has been assigned from analogy.

The action of chlorine and bromine on *o*-, *m*-, and *p*-fluorotoluenes has been tried either in the presence of iron or iodine as catalyst and the iodination generally effected in presence of a mixture of nitric and sulphuric acids or in presence of sodium nitrite and strong sulphuric acid (Varma and Panickar, *J. Indian Chem. Soc.*, 1926, **3**, 342; Varma and Narayan, *ibid.*, 1927, **4**, 283). *o*-Fluorotoluene on chlorination gives, 2-fluoro-5-chloro- (obtained in larger quantities) and 2-fluoro-6-chlorotoluene, the former is obtained from 2-fluoro-5-aminotoluene and the latter oxidised to 2-fluoro-6-chlorobenzoic acid, m.p. 190° (Lock, *Ber.*, 1936, **69B**, 2253). The corresponding bromo compounds are also described and their constitution assigned from analogy. 2-Fluoro- and 5-fluoro-5-iodo-, and 2-fluoro-6-iodo-toluenes are obtained from the iodination and they have also been prepared from the corresponding fluoro-amino-toluenes. In a similar way from *m*-fluoro-toluene, 3-fluoro-4-bromo, 3-fluoro-6-bromo-, 3-fluoro-4-iodo- and 3-fluoro-6-iodo-toluenes have been obtained. The constitutions have been assigned only from analagy and the compound obtained in larger proportion being taken to be the 6-substituted derivative. Some of the compounds have been oxidised to the corresponding benzoic acids. *p*-Fluorotoluene yields 4-fluoro-3-bromo-toluene, which has been oxidised to the corresponding

acid; 4-fluoro-2-iodo- and the already known 4-fluoro-3-iodotoluene, obtained previously from 3-iodo-4-aminotoluene (Yaun and Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 4426), have also been oxidised to the corresponding acids.

Only a few simple sidechain halogen derivatives of *o*-, *m*-, and *p*- fluorotoluenes are described in the literature. The fluorotoluenes, fluorobenzyl and -benzal halogen derivatives have been halogenated under varying conditions and many mixed halogen compounds have been obtained. The constitution of all these compounds has been determined by oxidising them to the corresponding fluorobenzoic acids.

E X R E R I M E N T A L

p-*Chlorofluorobenzene.*—Fluorobenzene (10 c.c.) and iron powder (0·5 g.) were taken in a flask with a reflux condenser and chlorine (1 mol.) was passed into it in a slow current with occasional shaking. The liquid was filtered, washed with a very dilute solution of sodium hydroxide and with water, dried over calcium chloride and distilled. The fraction (10·3 g.) distilling at 125-34° was collected separately and on redistillation gave a clear liquid boiling at 130°.

Dichlorofluorobenzene. (*i*) *From fluorobenzene.*—Chlorine (2 mols.) was passed into fluorobenzene (10 c.c.) and iron powder (0·5 g.) and the product worked up as above. The fraction (3·5 g.) distilling at 125-35° was found to be *p*-chlorofluorobenzene while the fraction distilling at 165-75° (11·8 g.) on redistillation gave a liquid boiling at 169-75°. This fraction seems to be a mixture of 2:4- and 3:4-dichlorofluorobenzene. Since the boiling points of the two liquids are very close together it was not possible to separate the two constituents by fractional distillation.

(*ii*) *From* p-*chlorofluorobenzene.*—*p*-Chlorofluorobenzene (10 c.c.) under similar conditions with chlorine (1 mol.) gave the mixture of dichlorofluoro derivatives (9·9 g.).

3:4-*Dibromofluorobenzene.*—To *p*-fluorobromobenzene (15 g.) and iron powder (1 g.) in a flask, bromine (4·5 c.c.) was added slowly and the solution refluxed on a water-bath for about 8 hours. After this period the product was washed as before and distilled under reduced pressure. The distillate (5·8 g.) solidified and was crystallised from rectified spirit as needles, m.p. 69°. (Found: Br, 64·12. $C_6H_3Br_2F$ requires Br, 62·96 per cent).

2:4-*Dibromofluorobenzene.* (*i*) *From* p-*bromofluorobenzene.*—The liquid product (11·8 g.) from the preceding experiment was redistilled under reduced pressure and a pure product, b.p. 109-12°/38 mm. was obtained. (Found: Br, 63·33. $C_6H_3Br_2F$ requires Br, 62·96 per cent).

(*ii*) *From 2:4-Dibromoaniline.*—2:4-Dibromoaniline (25 g.) (Chattaway and Clemo, *J. Chem. Soc.*, 1916, **109**, 91) was diazotised in the usual way at 0° to -5° and to the diazo solution 40% of hydrofluoboric acid (50 c.c.) added gradually with stirring and the precipitated fluoborate was washed with alcohol and ether, mixed with water (100 c.c.) and refluxed for about 6 hours when on cooling a dark brown liquid separated out. It was extracted with chloroform, washed, dried and distilled under reduced pressure. The fraction distilling at 75-90°/9 mm. was collected and it gave on redistillation a pure product, b.p. 103-105°/32 mm. or 214-16°/756 mm. It is a heavy oily liquid, colourless when pure. (Found: Br, 62·13. $C_6H_3Br_2F$ requires Br, 62·96 per cent).

p-*Iodofluorobenzene.*—Fluorobenzene (5 c.c.), iodine (6·5 g.), sodium nitrite (8 g.) and carbon tetrachloride (20 c.c.) were refluxed on a water-bath. Fuming sulphuric acid (20 c.c.)

was added drop by drop during an hour and the solution refluxed for 4 hours more, allowed to cool, poured into a large volume of water, dried and distilled. The fraction (9 g.) between 175-80° was collected and on redistillation it gave a light brown oil. b p. 178-81°/758 mm. Its constitution was established by converting it into 4:4-difluorodiphenyl in the following way.

p-Iodofluorobenzene (2 g.) and copper bronze (1 g.) were refluxed on a sand-bath at 200-20° for 6 hours. The product was extracted with ether, filtered and allowed to stand for some days when 4:4-difluorodiphenyl, m.p. 89°, separated out.

2-Fluoro-5-chlorotoluene.—Chlorine (1·3 mols) was passed slowly into a flask containing *o*-fluorotoluene (15 c.c.) and iron powder (0·3 g.) during a period of 5 to 6 hours with shaking. The products were washed repeatedly with water, dilute alkali solution, finally again with water, dried over calcium chloride and distilled. Unacted *o*-fluorotoluene distills at first at 95-125° and then two distinct fractions one (3·5 g.) distilling at 145-55° and the other (11·5 g.) at 155-60° were obtained. These fractions gave pure samples on redistillation. The first fraction was found to be 2-fluoro 6-chlortoluene, b. p. 151-52°/752 mm. It gives on oxidation 2-fluoro-6-chlorobonzoic acid, m.p. 159° (Hock, *Ber.*, 1936, **69B**, 2253). The second fraction on repeated distillation gives a pure product, b. p. 157-59°/752 mm. (Found: Cl, 24·6. C_7H_6ClF requires Cl, 24·56 per cent). The same compound was prepared from 2-fluoro-5-aminotoluene by diazotising with sodium nitrite and hydrochloric acid at 0° and treating the diazo product with cuprous chloride and concentrated hydrochloric acid. Both of these compounds give on oxidation the same 2-fluoro-5-chlorobenzoic acid, m. p. 168°. (Found: Cl, 20·30. $C_7H_4O_2ClF$ requires Cl, 20·34 per cent).

3-Fluoro-6-bromotoluene.—To a solution of *m*-fluorotoluene (15 c.c.) in carbon tetrachloride (20 c. c.) a solution of bromine (8 c. c.) in carbon tetrachloride (20 c. c.) was added in the presence of iron powder (0·5 g.) drop by drop under cooling and the solution allowed to stand overnight. The product was washed free of bromine, dried and distilled. Two fractions, one (5·2 g.) distilling between 160-75°/756 mm. and the other (18·7 g.) distilling between 175-85°/756 mm. were obtained. The latter fraction on repeated distillation gave 3-fluoro-6-bromotoluene, a colourless liquid, b. p. 177°/756 mm. (Found: Br, 42·43. C_7H_6BrF requires Br, 42·35 per cent). It is oxidised in the usual way by alkaline potassium permanganate to 3-fluoro-6-bromobenzoic acid, m. p. 151°, needle-shaped crystals, soluble in ether and alcohol. (Found: Br, 37·58. $C_7H_4O_2BrF$ requires Br, 36·51 per cent).

3-Fluoro-4-bromotoluene.—The first fraction in the above experiment distilling at 160-75° on redistillation gave pure 3-fluoro-4-bromotoluene, b. p. 169°/756 mm. (Found: Br, 42·13. C_7H_6BrF requires Br, 42·35 per cent).

3-Fluoro-6-iodotoluene.—To *m*-fluorotoluene (10 c. c.), iodine (13 g.) carbon tetra chloride (30 c. c.) and sodium nitrite (10 g.) in a flask, heated in a paraffin bath at 120-30° under reflux, fuming H_2SO_4 (20 c. c.) was added drop by drop for 2 hours, under shaking and the temperature of the bath raised to 160-70° and maintained for about 3 hours after the addition of the acid. The product was poured into water, washed, dried and distilled when the main product (12·5 g.) distilled at 135-45°/9 mm. On redistillation it gave 3-fluoro-6-iodotoluene, b. p. 138-39°/9 mm. (Found: I, 52·35. C_7H_6IF requires I, 53·80 per cent).

3-Fluoro-4-iodotoluene.—In the previous experiment the fraction distilling at 125-35° on repeated distillation yielded 3-fluoro-4-iodotoluene (2·3 g.), b. p. 138-39°/9 mm. (Found: I, 52·98. C_7H_6IF requires I, 53·80 per cent).

4-Fluoro-3-bromotoluene.—To a solution of *p*-fluorotoluene (10 c. c.) in carbon tetra chloride (15 c. c.) in a flask, iron powder (1 g.) and bromine (5 c. c.) in carbon tetrachloride (15 c. c.) were added when a vigorous reaction set in with evolution of hydrogen bromide. After the addition the product was allowed to stand for 24 hours, washed free of bromine and distilled. The fraction distilling at 174-80° (11 g.) was redistilled thrice when a colourless liquid, boiling at 174°-177°/757 mm. was obtained. (Found: Br, 42·46. C_7H_6BrF requires Br, 42·35 per cent).

4-Fluoro-3-bromobenzoic Acid.—4-Fluoro-3-bromotoluene (1 c. c.), potassium permanganate (0·8 g.) water and potassium hydroxide (10% solution, 2 c. c.) were heated under reflux for 30 hours and the acid formed isolated in the usual way. White crystalline solid, m. p. 156°, sparingly soluble in cold water, was obtained. (Found: Br, 36·42. $C_7H_4O_2BrF$ requires Br, 36·51 per cent).

2-Fluoro-5-iodotoluene.—(*i*) From 2-fluorotoluene.—*o*-Fluorotoluene (15 c. c.), carbon tetrachloride (40 c. c.), powdered iodine (20 g.) and sodium nitrite (15 g.) were refluxed on a paraffin-bath at 120°, while fuming sulphuric acid (25 c. c.) was added slowly in 2 hours. After this period, the temperature was raised and maintained at 150-60° for 2 hours. The product was cooled, washed free of iodine, dried and distilled when one fraction at 75-95°/8 mm. (13·8 g.) and another fraction (5·3 g.) at 105-25°/8 mm. were obtained. The first fraction when purified boils at 85°/8 mm. and is a light yellowish liquid. (Found: I, 53·28. C_7H_6IF requires I, 53·80 per cent).

2-Fluoro-6-iodotoluene.—The second fraction in the above experiment gives on repeated distillation a pure product boiling at 114-16°/8 mm. (Found: I, 53·28. C_7H_6IF requires I, 53·80 per cent).

2-Fluoro-5-aminotoluene.—Nitration of *o*-fluorotoluene (80 g.) with fuming nitric acid (88 c. c.) according to Schiemann (*Ber.*, 1929, **62 B**, 1795), gave 2-fluoro-5-nitrotoluene (52 g.) and 2-fluoro-6-nitrotoluene (16 g.). 2-Fluoro-5-nitrotoluene was reduced (Hock, *loc. cit*) when brownish black liquid, b. p. 85-86°/9 mm. was obtained. (Found: N, 11·11. C_7H_8NF requires N, 11·20 per cent). The hydrochloride melts at 220° with decomposition.

(*ii*) From 2-fluoro-5-aminotoluene.—2-Fluoro-5-aminotoluene (10 g.) was diazotised and treated with potassium iodide (15 g.) in water (25 c. c.). The dark heavy oil was washed free of iodine and distilled at 80-90°/9 mm. On redistillation it gave 2-fluoro-5-iodotoluene, b. p. 86-87°/9 mm.

2-Fluoro-6-iodotoluene from 2-fluoro-6-aminotoluene.—2-Fluoro 6-aminotoluene (7 g.) was diazotised and treated with potassium iodide (10 g.) dissolved in water (20 c. c.) and the oily product separated was purified and distilled at 117°/9 mm. as a heavy oily liquid.

o-, m- and p-Fluorobenzyl iodides.—These compounds were obtained by boiling the corresponding benzyl chlorides or bromides (5 g.) with potassium iodide (8 g.) and acetone (50 c. c.) under reflux for 4 to 5 hours. The product was then cooled, diluted with water, extracted with carbon tetrachloride, washed with sodium carbonate solution, filtered and distilled under reduced pressure. The benzyl iodides are brownish coloured liquids which distil under ordinary pressure with partial decomposition and have lachrymatric properties.

o-Fluorobenzyl iodide, b. p. 91°/8 mm. (Found: I, 54·36. C_7H_6IF requires I, 53·73 per cent).

m-Fluorobenzyl iodide, b. p. 98°/12 mm. (Found: I, 54·10. C_7H_6IF requires I, 53·73 per cent).

p-Fluorobenzyl iodide, b. p. 102-103°/9 mm. (Found : I, 54·76. C_7H_6IF requires I, 53·73 per cent).

These componnds on oxidation with potassium permanganate gave the corresponding fluorobenzoic acids.

m-*Fluorobenzal Chloride*.—Chlorine (2 mols.) was passed through *m*-fluorotoluene (10 c. c.) heated on a sand-bath and after 6 hours the product was extracted with carbon tetrachloride, washed, dried and distilled when one fraction at 170-85° and another at 185-200° were obtained. The former on redistillation gave *m*-fluorobenzyl chloride, b.p. 176°/756 mm. and the latter on repeated distillation gave *m*-fluorobenzal chloride, a colourless liquid with pronounced lachrymatric properties boiling at 195-97°/756 mm. (Found : Cl, 39·09. $C_7H_5Cl_2F$ requires Cl, 39·64 per cent).

m-*Fluorobenzal Bromide*.—It was obtained by adding bromine (1 mol.) to *m*-fluorobenzyl bromide or bromine (2 mols.) to *m*-fluorotoluene heated on a sand-bath and separated as before. Slightly brownish liquid, b. p. 108-10°/8 mm. was obtained. (Found : Br, 59·80. $C_7H_5Br_2F$ requires Br, 59·68 per cent).

o- *and* m-*Fluorobenzyl Chlorobromides*.—These compounds were prepared by adding bromine (1 mol.) to *o*- or *m*-fluorobenzyl chloride heated on a sand-bath or by passing a slow current of chlorine (1 mol.) through the corresponding bromides under the same conditions and the products isolated in the usual way.

o-*Fluorobenzal Chlorobromide*.—The fraction distilling at 100-20° was subjected to repeated distillation when brownish heavy liquid, b. p. 109-10°/7 mm., was obtained. (Found: total halogen, 51·76. C_7H_5BrClF requires total halogen, 51·65 per cent).

m-*Fluorobenzalchlorobromide*.—The fraction at 105-25° on repeated distillation gave a pure product, boiling at 111-13°/9 mm. It boils at 228-30°/756 mm. with slight decomposition. (Found : total halogen, 51·05. C_7H_5BrClF requires total halogen, 51·65 per cent).

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STUDIES ON THE PHOTOCHEMICAL ACTIVITY OF MIXTURES OF VANADIC ACID AND TARTARIC ACID. PART IV. PHOTOREDUCTION OF VANADIC ACID IN CIRCULARLY POLARISED LIGHT. INDUCED CIRCULAR DICHROISM

By T. L. Rama Char

The influence of *d*- and *l*- circularly polarised light on the photoreduction of vanadic acid sol by tartaric acid and of mixtures of sodium meta-vanadate and tartaric acid, has been studied. Differences in the velocity of the reaction and circular dichroism in the reaction product are observed It has also been found that reduced vanadic acid sol exhibits circular dichroism in the visible region on exposure to circularly polarised light.

The photoreduction of (*a*) vanadic acid (as meta-vanadate) by tartaric acid in ordinary light, and (*b*) circularly dichroic vanadic acid sol in circularly polarised light, has been described in the previous papers of this series (Rama Char, *J. Indian Chem. Soc.*, 1941, **18**, 507, 605). In the present investigation, the influence of circularly polarised light on (*i*) reaction (*a*), (*ii*) photochemically active systems containing undichroic vanadic acid sol, and (*iii*) reduced vanadic acid sol, has been studied.

A. *Photoreduction of Vanadic Acid Sol: Induced Dichroism*

The experimental arrangement, the method of preparation of the sol, etc., are the same as those described before (Rama Char, *loc. cit.*). The photoreduction was studied with freshly prepared sol as well as sol pre-excited in unpolarised light. Measurements of ellipticity (Rama Char, *ibid.*, 1941, **18**, 563) showed that the sol did not develop any dichroism on excitation in unpolarised light for 5 hours. The sol at p_H 5·3 was mixed with the reductant; after exposure to *d*- and *l*- circularly polarised light, the solutions were estimated for vanadium (V^5) and the dichroism (as ellipticity) measured. The reductants were recrystallised before use.

There is no dark reaction with mixtures of sol and tartaric acid. The results obtained for the velocity of the reaction in *d*- and *l*-lights are given below. dx/dt refers throughout to the number of g. mols transformed per minute.

Conc. of potassium tartrate = 0·10 *M*. Radiation = whole visible. p_H = 5·5. Temp. = 25°. Conc. vanadic acid sol = 0·05 *M*. Period of excitation of sol = 5 hours. $I_{abs.}$ = 1384 ergs (in all cases). Period of exposure of reaction mixture = 4½ hours. Intensity of exciting radiation for sol = 7784 ergs (Tables I and II)

Table I

Reaction mixture exposed to →	Unexcited sol. $dx/dt \times 10^5$. d-light.	Unexcited sol. l-light.	Sol excited in unpolarised light. $dx/dt \times 10^5$ d-light.	Sol excited in unpolarised light. l-light.
Reductant *d*-tartrate	1·94	1·39	2·08	1·53
l- ,,	1·94	1·34	2 13	1·57
dl. ,,	1·94	1·34	2·08	1·53
Racemic tartrate	1·94	1·39	2·04	1·53

Table II

Wave-length.	Length of solution.	Ellipticity developed on exposure to d-light.	Ellipticity developed on exposure to l-light.
5780 Å	4 cm.	−0·30°	—
5460	3	−0·80	−0·30°
5200	1	−0·50	−0 40
4916	0·2	−0·15	−0·10

The results show that, irrespective of the reductant used, the velocity of the reaction is greater in *d*-light than in *l*-light, whether the sol is unexcited or pre-excited in unpolarised light. The quantum efficiency γ of the photo-process is of the order of 0·4 (mean value). The corresponding values for the circular dichroism developed in these mixtures after exposure to *d*- and *l*-light are given above. The mixtures are not initially (*i.e.*, before reaction) dichroic, nor do they develop dichroism on keeping in the dark for 6 hours. Systematic measurements showed that, like the velocity of the reaction, the ellipticity developed in the reaction mixture is independent of (*i*) the nature of the reductant used, *d*-, *l*-, or racemic-tartrate, and (*ii*) whether the sol is unexcited or pre-excited in unpolarised light. As such the ellipticity values for a typical set of mixtures of sol and reductant are given throughout.

The ellipticity (Table II) has a negative sign, *i.e.*, the anisotropy factor is negative (Rama Char, *loc. cit.*), whether the mixture is exposed to *d*- or *l*-light; the magnitude is always greater for exposures to *d*-light, which gives the greater value for the reaction velocity, than to *l*-light. The observed dichroism lies in the yellow, green and blue regions which are effective for the photoreduction.

B. *Photoreduction of Mixtures of Sodium meta-vanadate and Tartaric Acid: Induced Dichroism*

For the reaction in the ultraviolet, circularly polarised light was obtained by the combination of a Glans polarising prism and a Carl-Zeiss quarter-wave plate. The velocity of the reaction in *d*- and *l*-light (visible and ultraviolet) is given below. T refers to the tartrate ion. There is no dark reaction.

TABLE III

Conc. of H_2T=0·05 *M*. Radiation=whole visible. Conc. $NaVO_3$=0·1 *M*. Period of exposure=6 hours. p_H=5·4. Temp.=25°. $I_{abs.}$=4583 ergs. (in all cases).

Polarised light	$dx/dt \times 10^5$ *d*-H_2T	*l*-H_2T	Racemic-H_2T	γ(mean value).
d-circular	2·91	2·91	2·91	0 35
l- ,,	2·22	2·22	2·22	

TABLE IV

λ=3660 Å (Schott and Gen ultraviolet filter). $I_{abs.}$=4065 ergs (in all cases). Other conditions same as in Table III.

Polarised light	$dx/dt \times 10^5$ *d*-H_2T	*l*-H_2T	Racemic-H_2T	γ (mean value)
l-circular	5·31	5·31	5·31	0·35
d- ,,	4·26	4·26	4·26	

For visible light, the velocity of the photoreduction is greater in *d*-light than in *l*-light, the reverse being the case in the ultraviolet, and in both cases it is independent of the reductant. Ghosh *et al* (*J. Indian Chem Soc.*, 1937, **14**, 495, 617) have found that in ultraviolet light, photochemical reactions using vanadic acid sol either as a photo-oxidant or as a sensitiser give a greater value for the velocity in *l*-light. The circular dichroism developed in the reaction mixture on exposure to visible light is independent of the reductant, *d*-, *l*- or racemic tartaric acid; the values for a typical set of mixtures are given below.

TABLE V

Conditions same as in Table III.

Wave-length.	Length of sol.	Ellipticity developed on exposure to. *d*-light	*l*-light.
5780 Å	3 cm.	−0·35°	—
5460	2	−0·63	−0·35°
5200	0 5	−0·84	−0·56
4916	0·1	−0·56	−0·35

The results are of the same type as those obtained in the photoreduction of vanadic acid sol. The wave-lengths in which dichroism is observed are effective for the photoreduction.

The influence of *d*- and *l*-circularly polarised visible light on the photoreduction at p_H 5·0 to 5·5 of undichroic vanadic acid sol as well as of vanadate-tartaric acid mixtures leads to some significant results. The velocity of the reaction and the circular dichroism (which is always negative) developed is (*i*) independent of the reductant, and (*ii*) greater for exposures to *d*-light than to *l*-light. These observations suggest the possibility that the dichroism developed in all the above cases is due to the action of *d*- and *l*-light on the reduced vanadic acid sol (or reduced vanadate-tartaric acid mixture) which is produced as a result of photoreduction : $V^5 \longrightarrow V^4$. The experiments that were carried out to test this hypothesis are described below.

C. *Induced Dichroism in Reduced Vanadic Acid Sol*

The complete reduction of 0·1*M* vanadic acid sol at p_H 5·3 was effected by exposing mixtures of sol and an excess of potassium racemic-tartrate (0·16*M*) or racemic-mandelate (0·16*M*) to light for 8 hours. The reduction of the sol by hydrazine hydrate was carried out in the dark. The reduced solutions were estimated to ensure complete reduction. These solutions have no dichroism in visible light, nor do they develop any on keeping in the dark for 5 hours. But dichroism is induced in them on exposure to *d*- and *l*-light ; the results are given below ; titrations performed after exposure showed that there was no change in the concentration of the sol.

TABLE VI

Conc. of reduced vanadic acid sol = 0·05 *M*. Radiation = whole visible. Period of exposure of sol = 5 hours. Intensity of exciting radiation = 7784 ergs (in all cases). (*a*) Sol reduced by racemic tartrate ; (*b*) sol reduced by racemic mandelate ; (*c*) sol reduced by hydrazine hydrate.

		Ellipticity developed on exposure to			Ellipticity developed on exposure to			Ellipticity developed on exposure to	
Wave-length.	Length of solution.	*d*-light.	*l*-light.	Length of solution.	*d*-light.	*l*-light.	Length of solution.	*d*-light.	*l*-light.
(*a*) 5780 Å	4 cm.	−0·12°	−0·09°	(*b*) 3 cm.	−0·48°	−0·32°	(*c*) 3 cm.	−0·90°	−0·60
5460	4	−0·15	−0·09	2	−0·48	−0·32	2	−0·90	−0·60
5200	3	−0·18	−0·12	2	−0·80	−0·56	1	−0·75	−0·50
4916	2	−0·09	−0·06	1	−0·24	−0·16	1	−0·45	−0·30

Dichroism is developod irrespective of the reductant used for reducing the sol. The ellipticity (just as in sections A and B) is always negative and is greater for exposures to *d*-light. The wave-length region in which dichroism is observed is the same as in sections A and B.

The observations made in sections A, B and C indicate that the induced dichroism that is observed in sections A and B is due to the action of *d*- and *l*-light on the reduced sol that is produced as a result of photoreduction. The induced dichroism leads to differences in light absorption and therefore to differences in reaction velocity in *d*- and *l*-light.

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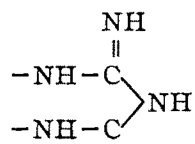
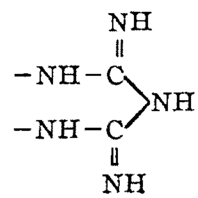
22	Fig. 5	Ascorbic acid $= 1 \times 10^{-2} M$	Ascorbic acid $= 2 \times 10^{-2} M$
43	Line 4	N, 4·88	H, 4·88
,,	Below line 12		

ESTIMATION OF BISMUTH. PART I. GRAVIMETRIC ANALYSIS WITH PHENYLARSONIC ACID

BY ANIL KUMAR MAJUMDAR

Bismuth phenylarsonate is practically insoluble in water. It has been shown that it can be quantitatively precipitated at a p_H (5·1–5·33) from a solution containing acetic acid buffered with sodium or ammonium acetate. Methods for the estimation and separation of bismuth from salts of thallium(*ous*), alkalis, alkaline earths (*e g.*, calcium strontium, barium, magnesium), copper, silver, lead, mercury, cadmium, cobalt, nickel, zirconium, thorium and tin as also in presence of sulphate ions have been described.

During the last few years a number of methods for the determination of bismuth has been described. These are, however, often complicated or involved the use of costly reagents. It is well known that the phosphate and arsenate of bismuth are sparingly soluble. Attention was directed to organic arsenical derivatives with the expectation that the precipitate would improve in quality and purity and might be of definite composition and suitable for direct weighing. These criteria were realised in the phenylarsonic acid compound. This acid is readily prepared in good yield by the method of Palmer and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 1361).

Bismuth has been estimated by this reagent both gravimetrically and volumetrically with excellent results. In an acetic acid solution, buffered with sodium or ammonium acetate, it gave an insoluble basic salt of the composition $C_6H_6AsO_4Bi$ in which the percentage of bismuth was only 49·06. This compound of bismuth was found to be soluble in excess of dilute mineral acids or acetic acid and to decompose into hydroxide in presence of dilute alkali or ammonia.

Besides forming a basic compound with bismuth, it formed, with other common elements, compounds which were found to be more or less soluble in mineral acids or acetic acid.

Mercury(*ic* and *ous*), cadmium and lead ions gave white precipitates, and cupric, a greenish white with the reagent solution in water. With ferric ion, a cream coloured, with cobaltous, a red, and with aluminium, zinc, silver and manganese, white precipitates in presence of sodium acetate were obtained. The precipitates due to cobalt, silver, mercury (*ic*), cadmium, zinc and copper were soluble in potassium cyanide. The mercurous compound dissolved in potassium cyanide or ammonium acetate solution with the usual separation of metallic mercury. Mercury (*ic*) and lead compounds were further soluble in solutions of ammonium acetate. Thallous, alkali and alkaline earth salts gave no precipitate with the reagent even in presence of sodium or ammonium acetate.

Bismuth has been separated from silver, copper, cadmium, cobalt and nickel in presence of potassium cyanide and from mercury(*ic*) and lead in presence of ammonium acetate. Since the reagent precipitates quantitatively zirconium, thorium and tin in acid solutions and bismuth phenylarsonate remains in solution in presence of acids, bismuth has been easily estimated in the filtrates obtained after the separation of the said metals by the methods outlined below. Bismuth can also be estimated in presence of sulphate ions. The estimation may further be conducted even in presence of salts of alkalis and of alkaline earths (Ca, Sr, Ba, Mg etc.), for they do not produce a precipitate with the reagent.

EXPERIMENTAL

Preparation of the Reagent.—The reagent was prepared according to the method submitted by Bullard and Dickey ("Organic Synthesis", 1935, Vol. XV, p. 59). The light yellow crystals obtained were crystallised from water, using decolourising carbon, and recrystallised to free it from traces of chloride. The melting point of the crystal was 156-57° with decomposition and the yield was about 47% of the theoretical.

Composition of the Bismuth salt of Phenylarsonic Acid.—Bismuth subnitrate (Kahlbaum) was dissolved in nitric acid and reprecipitated with water and dissolved in the least quantity of nitric acid (*pro analysi*). To this solution, diluted with a large volume of water, was added an excess of the reagent solution and a few grams of sodium acetate and boiled for some time with stirring till the precipitate became crystalline. The solution was filtered, washed with hot water till free from excess of the reagent and dried at 110° for an hour.

For the determination of composition, a weighed quantity of the sample so prepared, was slowly ignited in a porcelain crucible over Bunsen burner, dissolved in hydrochloric acid and diluted such that the solution was 0·3*N* in acid. The solution was saturated with hydrogen sulphide, heated to coagulate the precipitate, filtered and washed with a solution of sodium sulphide. The sulphide precipitate was then dissolved in nitric acid and the bismuth was determined as phosphate according to the method of Schoeller and Waterhouse (*Analyst*, 1920, **45**, 435) as the weighed sample contained less than 0·1 g. of bismuth (Schoeller and Lambie, *Analyst*, 1937, **62**, 533). (i) Wt. of sample=0·0880 g.; Wt. of $BiPO_4$=0·0626 g. and therefore bismuth=48·9%.

A tentative suggestion for the formula of the bismuth compound was $C_6H_5AsO_3 \cdot Bi(OH)$ which contains 49·06% of bismuth.

Reagents.—In the estimations, all reagent quality chemicals were used except where specifically mentioned. Reagents were: prepared and crystallised phenylarsonic acid (1g. in 100 c. c. water), a 10% solution of sodium acetate in water and a 10% solution of ammonium acetate in water and acetic acid about 2*N*.

Standard Solutions

Bismuth subnitrate was dissolved in concentrated nitric acid and made up to a definite volume with water. The bismuth content of the solution per c.c. was determined by taking a definite quantity of the solution in a weighed porcelain crucible, evaporating to dryness and igniting it to oxide (Miller and Van Dyke Cruser, *J. Amer. Chem. Soc.*, 1905, **27**, 116). The bismuth content was further checked by estimating as phosphate (Schoeller and Waterhouse, *loc. cit.*)

Copper.—Electrolytic copper was dissolved in nitric acid and diluted with water to a definite volume. A measured quantity of the solution was fumed with concentrated H_2SO_4 and the copper content determined electrolytically.

Cadmium.—Kahlbaum's purest quality cadmium carbonate was dissolved in nitric acid and made up to a desired volume with water. From a definite amount of the solution cadmium was estimated as sulphate.

Mercury.—Mercurous nitrate was converted to mercuric nitrate by repeated evaporation with concentrated nitric acid and then diluted with water to a certain volume. The mercury content of the solution per c. c. was determined as sulphide by Volhard's method.

Silver.—Silver nitrate was dissolved in a definite amount of water whose silver content was determined as chloride from an aliquot part of the solution.

Cobalt.—Kahlbaum's 'nickel free' cobalt nitrate was dissolved in a certain volume of water. From a measured quantity of this solution cobalt was estimated as sulphate.

Nickel.—A solution was prepared with 'cobalt free' nickel nitrate of Kahlbaum and by the oxime method its amount of nickel was determined from a measured quantity of the solution.

Sulphate.—Hydrated sodium sulphate was ignited in a platinum basin to anhydrous salt. Weighed quantities of this anhydrous salt were used during the experiments.

Zirconium.—Kahlbaum's pure zirconium nitrate was treated with a few c. c. of conc. HCl and then diluted with water to a desired volume. From a measured amount of this solution, zirconium was determined by the methods of James, Fogg and Rice (*J. Amer. Chem. Soc.*, 1926, **48**, 895).

Thorium.—A thorium nitrate solution was prepared from Kahlbaum's pure quality sample and its amount of thorium determined, according to the method of James, Fogg and Rice (*loc. cit.*) from a measured quantity of the solution.

Tin.—A stannous chloride solution was prepared in water with a few c. c. of conc. HCl and its amount of tin, as oxide, was determined according to the methods of Knapper, Craig and Chandlee (*J. Amer. Chem. Soc.*, 1933, **55**, 3945) from a definite amount of the solution.

Lead.—Standard solution of lead from lead acetate was prepared and its lead content, per c. c. was determined as sulphate.

Estimation of Bismuth

I. To a nitric acid solution of bismuth was added an excess of the reagent solution, diluted to 250 c. c., and a few c. c. of sodium acetate to neutralise the mineral acid. The mixture was boiled with stirring till the precipitate, which was at first gelatinous, became crystalline. If the precipitate was found to remain gelatinous, a little excess of sodium acetate should be added. A large excess of sodium acetate or prolonged boiling with excess of sodium acetate should be avoided, as these led to low results possibly due to the decomposition of the precipitate to oxide. The precipitate was then allowed to settle, filtered hot through Gooch crucible and washed with hot water. Six or seven washings after transferring on the Gooch was found to free the precipitate from the excess of sodium acetate or the reagent. This was then dried at 110-120° and weighed. The amount of bismuth was found by multiplying the weight of the bismuth compound with the factor 0·4906.

The results are given in Table I.

TABLE I

No.	Bi taken.	Reagent added.	Sodium acetate.	Bi found.
1	0·04733 g.	15 c.c.	20 c c.	0·04743 g.
2	0·0757	25	20	0·0760
3	0·02367	10	10	0·02374
4	0·09466	40	40	0·09517
5	0·1183	50	40	0·1181
6	0·04733	25	50	0·04720

TABLE II

No.	Bi taken.	Reagent added	Bi found
1	0·04733 g.	20 c.c.	0·04730 g
2	0·0568	25	0·0568
3	0·09466	40	0·09504
4	0·03084	10	0·03081
5	0·1233	30	0·1233

II. An excess of the reagent solution was added to a solution of bismuth containing some free nitric acid. The solution was then neutralised with dilute ammonia (about $2N$) using

Wesselow's indicator, and after acidifying it with dilute acetic acid a slight excess (2 c. c.) of this acid and ammonium acetate solution (20 c.c.) were added. A large excess of acetic acid solution or ammonium acetate should be avoided. The mixture was diluted to 250 c.c. and boiled with stirring till the precipitate became crystalline. The precipitate was allowed to settle, filtered, washed and dried as mentioned above. The results appear in Table II.

Solubility in water.—To examine the solubility of the bismuth salt of phenylarsonic acid in water a weighed quantity of the bismuth precipitate in a gooch crucible dried at 110°-120° was washed twice with 400 c.c. portions of hot water, again dried and weighed. Practically there was no loss in weight. The compound is insoluble in water.

The total washings were evaporated to a small volume and no precipitation or colouration was observed when this was saturated with hydrogen sulphide.

Determination of p_H.—For the determination of p_H bismuth was precipitated by both the procedures. The p_H of the first filtrates from both, was determined with quinhydrone electrode and found to be between 5·1 to 5·33.

TABLE III

Procedure I.					Procedure II.			
Bi taken.	Reagent added.	Sodium acetate.	Bi found.	p_H.	Bi taken	Reagent added.	Bi found.	p_H.
0·0252 g.	10 c.c.	10 c.c.	0·02516 g.	5·16	0·0252 g	10 c.c.	0·02521 g.	5·22
0·0252	10	10	0·02521	5·1	0·0252	10	0·02521	5·33

The Estimation of Bismuth in presence of Sulphate Ions.—An excess of the reagent solution was added to a solution of bismuth and sodium sulphate, containing sufficient nitric acid to keep the precipitated sulphate in solution. If any precipitate separated due to the addition of the reagent, that was dissolved by warming with a few c.c. of nitric acid. The solution was then cooled, neutralised with dilute ammonia (2*N*) using Wesselow's indicator, acidified with the dilute acetic acid, 2 c.c. excess of which were added. After the addition of 20 c.c. of ammonium acetate solution it was diluted to 250 c.c. and then the usual procedure followed. If the precipitate formed after the addition of the reagent was not dissolved by nitric acid but kept as such, it was found to be contaminated with the sulphate ions. Results appear in Table IV.

TABLE IV

No.	Bi taken.	Sodium sulphate taken.	Reagent added.	Bi found.
1	0·03084 g.	1 g.	10 c.c.	0·03081 g.
2	0·03084	3	10	0·03081
3	0·03084	6	10	0·03091
4	0·1790	5	50	0·1789

TABLE V

Cu and Bi taken.		Reagent added.	Bi found
Bi	Cu.		
0·04733 g	0·1035	20 c c.	0·04724 g
0·02367	0·1035	10	0·02365
0·04733	0·05175	20	0·04730
0·02367	0·3105	10	0·02374

The bismuth precipitates (Table IV) after the weighings were dissolved in hot dilute hydrochloric acid and were diluted to large volumes. To these solutions were added normal barium chloride solutions (a few c.c.) but no turbidity or opalescence due to the precipitations of barium sulphate were observed. This showed that the precipitates of bismuth were completely free from sulphate ions.

Separation of Bismuth from Copper, Silver, Cadmium, Cobalt and Nickel.—To a nitric acid solution, containing bismuth and any of the mentioned cation, was added an excess of the reagent for the complete precipitation of bismuth The solution was then neutralised with dilute ammonia and then an excess of potassium cyanide sufficient to keep the other cations in solution added. The solution was acidified with dilute acetic acid just to acidity (using Wesselow's

indicator) then 2 c.c. excess of this acid along with 10 c.c. of ammonium acetate solution added, diluted to 250 c.c. and the usual way followed. Results appear in Tables V—IX.

TABLE VI

No.	Ag and Bi taken. Bi.	Ag.	Reagent added.	Bi found.
1	0·03084 g.	0·2122	15 c.c	0·03091 g.
2	0·03084	0·05305	15	0·03086
3	0·06167	0·05305	20	0·06162

TABLE VII

No.	Cd and Bi taken. Bi.	Cd.	Reagent added	Bi found.
1	0·03084 g	0·0553	10 c.c.	0·03086 g
2	0·03084	0·3318	15	0·03081
3	0·03084	0·1659	15	0·03091

TABLE VIII

No.	Co and Bi taken. Bi.	Co.	Reagent added.	Bi found.
1	0·03084 g.	0·0516	10 c.c.	0·03081 g.
2	0·03084	0·2064	15	0·03076
3	0·02238	0·2064	10	0·02237

TABLE IX

No.	Ni and Bi taken. Bi.	Ni.	Reagent added.	Bi found.
1	0·03084 g.	0·0603	10 c.c.	0·03086 g.
2	0·02238	0·2412	15	0·02227
3	0·02238	0·0603	15	0·02242

In the filtrates copper, silver, cadmium, cobalt and nickel might be estimated by decomposing the cyanide with mineral acid and then precipitating out the above elements as sulphides.

Separation of Bismuth from Zirconium and Tin

From a mixed solution of bismuth and zirconium or bismuth and tin, containing 5% by volume of hydrochloric acid, zirconium was precipitated by the reagent solution (1%) by the method of James, Fogg and Rice (*loc. cit.*), and tin by that of Knapper, Craig, and Chandlee (*loc. cit.*). The zirconium precipitate was washed with 1% hydrochloric acid and the tin with 4% solution of ammonium nitrate. The respective filtrates together with the respective washings were evaporated to dryness and fumed with the least quantity of concentrated sulphuric acid. The dried residues were then dissolved in water with a few drops of concentrated nitric acid to prevent hydrolysis. From these solutions bismuth was determined by the method followed for the estimation of it in presence of the sulphate ions. Results are given in Table X.

TABLE X

	Metals taken.		Reagent added.	Bi found.
1	Bismuth	0·02238g.	20 c.c.	0·02237g.
	Zirconium	0·05		
2	Bismuth	0·02238	20	0·02242
	Zirconium	0·05		
3	Bismuth	0·02238	15	0·02242
	Tin	0·0532		
4	Bismuth	0·04476	20	0·04474
	Tin	0·0532		

TABLE XI

	Metals taken.		Reagent added.	Bi found.
1	Bismuth	0·02238g.	15 c.c.	0·02232g
	Thorium	0·0525		
2	Bismuth	0·04476	20	0·04464
	Thorium	0·0525		

Separation of Bismuth from Thorium

From a hot solution (400 c.c.) of bismuth and thorium nitrates containing 75 c.c. of glacial acetic acid and 5 g. of ammonium acetate, thorium was first precipitated out, like zirconium and tin, by the methods of James, Fogg and Rice (*loc. cit.*), adding dropwise the prepared reagent solution (1%). The thorium precipitates were filtered off, washed and dissolved in 30 c.c. (1:1) hydrochloric acid and reprecipitated (*loc. cit.*), with the addition of a few c.c. more of the reagent solution, as the first precipitate was found to be contaminated with slight traces of bismuth. The precipitate was washed several times with water. The total filtrate was evaporated to dryness, fumed with the least quantity of concentrated sulphuric acid and the bismuth estimated according to the method given under 'The estimation of bismuth in presence of sulphate ions.' Results appear in Table XI.

In the presence of small quantities of bismuth, reprecipitation was not necessary. The filtrate on drying was directly used for the estimation of bismuth by dissolving in water with a few drops of concentrated nitric acid.

Separation of Bismuth from Mercury.—An excess of the reagent solution was added to a solution of bismuth and mercury containing some free nitric acid. This was diluted to 250 c.c. with water, 10 c.c. of ammonium acetate solution were added and boiled with stirring. If the precipitate was not crystalline a further quantity should be added till the precipitate became so. It was then filtered hot, washed and dried in the usual way. Results appear in Table XI.

TABLE XII

	Hg and Bi taken. Bi.	Hg.	Reagent added.	Am. acetate.	Bi found
1	0·0252g.	0·0503	10 c.c.	20 c.c.	0·0252g.
2	0·0252	0·1006	10	30	0·02526
3	0·0252	0·2012	10	40	0·0252

TABLE XIII

Pb and Bi taken. Bi.	Pb.	Reagent added.	Am. acetate.	Sodium acetate.	Bi found.
0·03084g.	0·1424	15 c.c.	50 c.c.	10 c.c.	0·03076g.
0·03084	0·2848	15	60	10	0·03091
0·03084	0·0712	15	40	5	0·03081

Separation of Bismuth from Lead

A solution of lead acetate was added to a solution of bismuth nitrate and a few c.c. of nitric acid also added to dissolve any precipitate formed. After the addition of some excess of the reagent solution it was neutralised with dilute ($2N$) ammonia and acidified with the dilute acetic acid (using Wesselow's indicator). Excess of this (2 c.c.) acid and 20 c.c. of ammonium acetate solution were then added, diluted to 250 c.c. and boiled with stirring. Some more of the ammonium acetate solution along with a little quantity of sodium acetate, which helped the crystallisation, were added till the precipitate was crystalline. The precipitate was then filtered, washed, dried and weighed as usual. Results are given in Table XIII.

Interfering Ions

Anions like citrate, tartrate, oxalate, etc., which form complexes with bismuth should be absent otherwise the reagent would not produce a precipitate of bismuth. Phosphates, arsenates, fluorides etc., that form sparingly soluble salts of bismuth should likewise be absent. The presence of chloride ions always gave very low results, and so the chlorides should be removed by repeated treatment with concentrated nitric acid or fuming with concentrated sulphuric acid. Since the reagent precipitates salts of iron, aluminium, beryllium, uranium and titanium in presence of sodium or ammonium acetate, all these salts should be removed. Chromium which under similar conditions contaminates the bismuth compound of the reagent should be separated. Due to the instability of the cyanide complexes of zinc and manganese the metals could not be separated from bismuth.

Antimony also should not be present, as to keep it in solution, excess of mineral acid was required. Mercury (*ous*) should be converted to mercury (*ic*) as in the presence of ammonium acetate, some metallic mercury was precipitated.

The volumetric estimation of bismuth by this reagent will shortly be published.

My best thanks are due to Prof. P. Rây for the facilities received in working out this piece of work in his laboratory.

N. B.—Out of a large number of agreeing results with varying proportions of the elements some are recorded in the paper. (Editor.)

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VISCOSITY OF AQUEOUS SOLUTIONS OF CALCIUM CHLORIDE AT 35°

By T. Patnaik and B. Prasad

Viscosity and density of aqueous solutions of calcium chloride have been measured. Viscosity of the solutions obey Jones and Dole equation. The divergence of the calculated value of A (0·016)' from that of the observed one (0·014) is not appreciable.

The present work is a continuation of the work on viscosity of strong electrolytes by Chacravarty and Prasad (*J. Indian Chem. Soc.*, 1938, **15**, 479 ; *Trans. Faraday Soc.*, 1939, **35**, 1466). The object is to find out the concentration limit to which Jones and Dole equation applies to calcium chloride which is a highly hydrated salt.

Experimental

Calcium chloride of 'Analar' quality of B. D. H. was used for the experiments. A stock solution was prepared and its strength was determined by finding out the concentration of the chloride ion as described before (*loc. cit.*). All the solutions used in the experiments were made by diluting the stock solution to the requisite volume. The error in concentration measurement is expected to be less than 1%. Double distilled water was used for making the solutions. The viscometer was of the same type as used by Chacravarty and Prasad (*loc. cit.*). The experimental procedure was of the same type as described in the papers referred to, except that a new arrangement was made for ensuring the same position of the viscometer in all the experiments and a microscope giving a magnification of 10 at a distance of 1 foot was used for adjusting the level of the liquid in the wider limb of the viscometer. The thermostat was maintained at 35°±0·005. No kinetic and surface tension correction was deemed necessary on account of the construction of the viscometer. The time of efflux for water was about 31 minutes. Five readings of time of flow seldom differing from one another by more than 0·2 second and two readings for the mass of the solution differing from each other by less than 0·001 g. were taken in the case of every solution. Verner time switch was used for recording the time. The error in relative viscosity (η/η_0) is not expected to exceed 0·003 in any one of the experiments.

A pyknometer of 55 c.c. capacity and of the same form as described in the papers referred to was used. The maximum error in specific gravity ($S=\frac{\text{density of solution}}{\text{density of water}}$ at the same temperature) is not likely to exceed twenty in a million in any case. The results are tabulated below. Concentration means gram moles per litre. The specific gravities have been calculated after applying necessary bouyancy corrections.

$$\frac{\eta}{\eta_0}=1+A\sqrt{c}+Bc. \qquad A=0{\cdot}014. \quad B=0{\cdot}034.$$

Conc.	S.	$\frac{\eta}{\eta_0}$ (obs.)	$\frac{\eta}{\eta_0}$ (calc.)
0·001	1·000081	1·0008	1·0008
0·002	1·000150	1·0016	1·0014
0·003	1·000230	1·0019	1·0018
0·005	1·000370	1·0026	1·0027
0·00625	1·000453	1·0033	1·0033
0·00715	1·000537	1·0040	1·0038
0·00875	1·000670	1·0046	1·0043
0·010	1·000760	1·0050	*1·0048*
0·020	1·001467	1·0077	1·0088
0·030	1·002270	1·0128	1·0127
0·050	1·003836	1·0185	1·0201

A and B are found out by the usual method. The calculated (0·016 from Falkenhagen-Vernon equation) and observed (0·014) values of A are in good agreement. The limit to which the Jones and Dole equation applies as shown by italics is much lower than in other cases most probably due to the high degree of the hydration of the salt.

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LIGHT ABSORPTION OF NICKEL ACETATE AND NICKEL PERCHLORATE

By K. Veeraiah and M. Qureshi

Light absorption of nickel acetate and nickel perchlorate in aqueous solutions has been studied spectrophotometrically in the visible region between 430 mμ and 760 mμ at different concentrations. In the case of nickel acetate, the molecular extinction coefficient curve shows continuous absorption in the violet region and a maximum absorption in the red at about 715 mμ. Dilution of the solution results in an increase in the molecular extinction coefficient at all wave-lengths, but this increase is more marked in the region of maximum absorption at the red end than in the region of continuous absorption at the violet end. The effect of dilution has been explained. In the case of nickel perchlorate, the general form of the absorption curve remains the same as with nickel acetate, but there is a distinct shifting of the band maximum towards shorter wave-lengths on dilution. The comparison of the two salts brings out the influence exerted by the anions on light absorption.

Several workers have studied the light absorption of nickel salts. Much of the early work, however, was of a qualitative nature. Hartley (*Sci. Trans. Roy. Soc. Dublin*, 1900, **7**, 253) studied the absorption spectra of coloured salts including those of nickel with special reference to the effect of dilution and rise of temperature on light absorption. The change of absorption on dilution of saturated solutions of deliquescent salts was attributed to the formation of molecules of more complex hydrated compounds. Müller (*Ann. Physik*, 1903, *iv*, **12**, 767 ; 1906, *iv*, **21**, 515), as a result of quantitative work in this field, observed that there was uniformity in the absorption of nickel salts in dilute aqueous solutions but the concentrated solutions had different tints and the colour of those salt solutions for which Beer's law was fulfilled within the limits of the visible spectrum was found to be independent of the temperature. Houstoun and co-workers (*Proc. Roy. Soc. Edin.*, 1913, **33**, 137, 156); studied the light absorption of nickel salts in aqueous and non-aqueous solutions in the visible and ultra-violet light. They found that the absorption was much greater in the case of non-aqueous solutions such as those in acetone or alcohol. Houstoun and Cochrane (*ibid.*, 1913, **33**, 147) obtained absorption curves for nickel sulphate and nickel acetate in the visible region and observed that the two curves are similar but the absorption of nickel acetate was slightly greater than nickel sulphate throughout the visible. Datta and Deb (*Phil. Mag.*, 1934, *vii*, **20**, 21) studied the absorption spectra of paramagnetic halides of the iron group, (including that of nickel chloride), and their solutions at different temperatures in water, ethyl alcohol and concentrated hydrochloric acid. Kahanowicz (*Z. Physik*, 1931, **68**, 126) obtained the extinction coefficients for infinitely dilute electrolytic solutions containing nickel and other metals throughout the visible spectrum. Von Koczkis (*Z. Physik*, 1930, **59**, 274) found that Lambert-Beer law holds for nickel chloride.

The present investigation was undertaken to make a study of the effect of dilution on the light absorption of nickel salts. The nickel salts selected for the present study were nickel acetate and nickel perchlorate on which little work of a quantitative and systematic nature has so far been done.

Experimental

In all the experiments mentioned below nickel acetate and nickel perchlorate of high purity, prepared according to the methods described, were made use of and solutions of different

concentrations were prepared in conductivity water. The extinction coefficients were measured with a Hilger Nutting spectrophotometer.

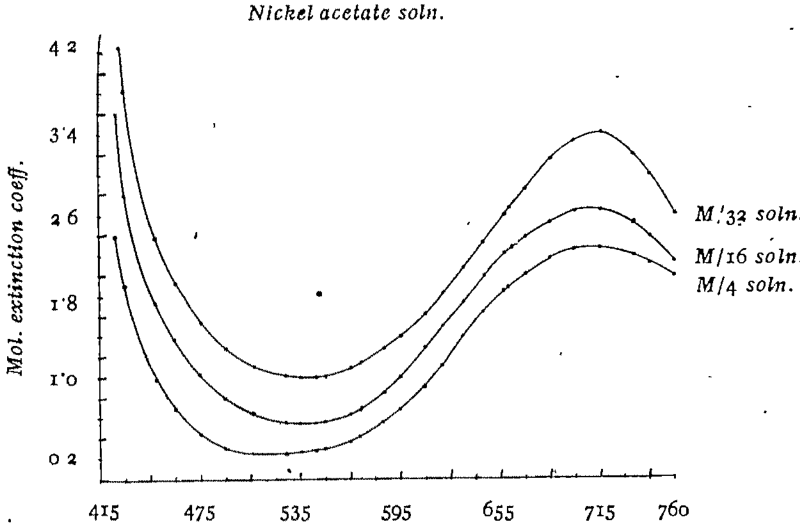
Preparation of Nickel Acetate.—Chemically pure acetic acid supplied by Merck was used in the preparation of nickel acetate. Pure basic nickel carbonate (Merck) was dissolved in slight excess of acetic acid. The solution was heated on a water-bath and small quantities of nickel carbonate were added gradually until no more of CO_2 was evolved. The excess of carbonate was removed by filtration and the filtrate left at room temperature to undergo slow evaporation. In a fortnight's time beautiful green crystals of nickel acetate separated out. The crystals were washed with water and recrystallised to obtain a pure sample of the salt. The pure salt on analysis closely corresponded to the formula $Ni(CH_3COO)_2, 4H_2O$.

Preparation of Nickel Perchlorate.—Pure basic nickel carbonate supplied by Merck was dissolved in a solution of pure perchloric acid and the mixture heated on a water-bath, until the reaction was complete. The excess of basic nickel carbonate was removed by filtration and the filtrate heated to 110° to expel excess of the acid. The solution was kept in vacuum over calcium chloride for several days for crystallisation. After a week's time, the salt separated out in long green needles. The crystals are highly hygroscopic and soluble in water, in alcohol and acetone. The salt was recrystallised twice to get a pure sample. The analysis of the salt showed that its composition corresponded to the formula $Ni(ClO_4)_2,6H_2O$. The melting point of the salt was found to be 200° corresponding to that obtained by Benrath, Hontung and Wilden (*J. prakt. Chem.*, 1930, **143**, 298).

Absorption Spectra.—Nickel acetate solutions of $M/4$, $M/16$ and $M/32$ strengths were prepared in conductivity water, and immediately after the preparation of each solution its light absorption was measured in the visible region by means of Hilger-Nutting spectrophotometer. Care was taken to screen the tube from light during two successive readings. The temperature of the solution was nearly 30°. The results which represent the mean of several readings are represented in Fig. 1.

FIG. 1

Nickel acetate soln.

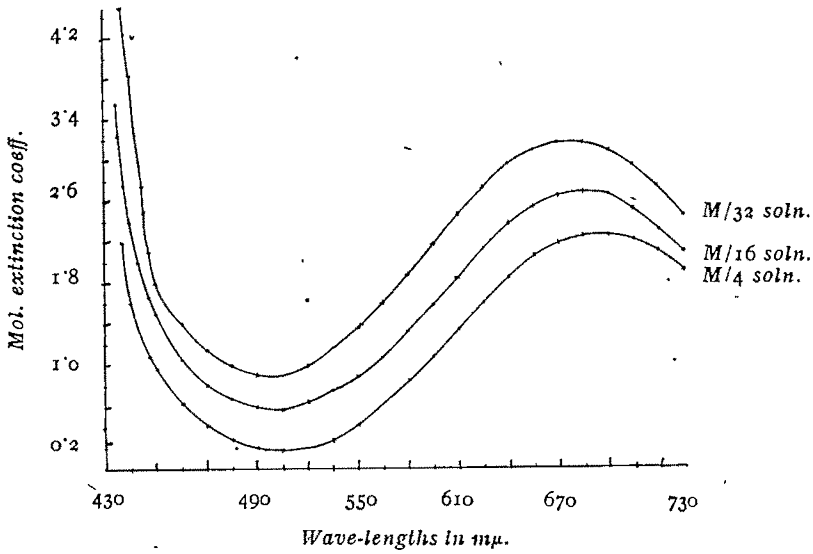


In the case of nickel perchlorate, solutions of the same strengths were employed. The rest of the procedure was also the same as in the case of nickel acetate. The extinction coefficients at various wave-lengths are recorded graphically in Fig. 2.

For comparison, the extinction coefficient curves of nickel acetate and nickel perchlorate are drawn in Fig. 3. A 2 cm. tube was used for measurement of extinction coefficients throughout.

FIG. 2

Nickel perchlorate soln.



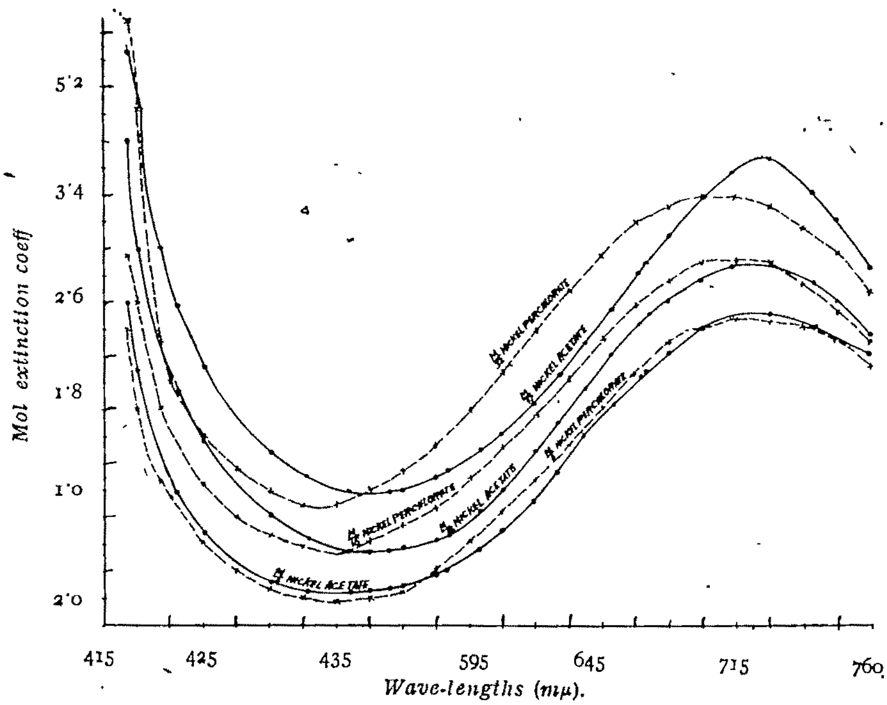
DISCUSSION

From Fig. 1, it is seen that nickel acetate shows continuous absorption in the violet region and a maximum absorption in the red at about 715 mμ. Dilution of the solution results in an increase in the molecular extinction coefficient at all wave-lengths, but this increase is more marked in the region of maximum absorption at the red end than in the region of continuous absorption at the violet end. There is no appreciable change in the position of the band. The effect of dilution on the extinction coefficient may be explained in more than one way. One possible reason for this effect may be the gradual elimination of the influence exerted by the negative ions on the absorption of the nickel ion due to dilution. The other and more probable reason is the progressive hydration of nickel ion brought about by dilution, resulting in an orientation of an increasingly larger number of water molecules round the ion, previous to the actual formation of nickel hydroxide.

In the case of nickel perchlorate, there is a continuous absorption at the violet end and a maximum absorption in the red region of the visible spectrum at about 715 mμ with $M/4$ solution (Fig. 2). In this case, also, dilution causes an increase in the extinction coefficient throughout the range of the visible spectrum, although this increase is more marked in the region of the maximum absorption than in the region of continuous absorption at the violet end. With nickel perchlorate, however, there is a distinct shifting of the band maximum towards shorter wave-length on dilution, which indicates a change in the nature of the absorbing entity. Nickel perchlorate, being a highly hygroscopic substance, will form a number of complex hydrated compounds on dilution, which may lead to a slight change in the quality and quantity of absorption. Apart from this, nickel ions in a solution of nickel perchlorate may also undergo progressive hydration on dilution as mentioned above in the case of nickel acetate.

FIG. 3

Absorption curves of nickel acetate and perchlorate



The absorption curves for nickel perchlorate show a remarkable similarity to those for nickel acetate (Fig. 3), particularly at higher concentrations. The points of maximum absorption in both cases lie at about 715 mμ at $M/4$ dilution. However, at $M/16$ and $M/32$ dilutions, the points of maximum absorption for nickel perchlorate shift gradually towards the shorter wave-lengths, while the points of maximum absorption for nickel acetate remain stationary. This shows that the negative ion exerts no appreciable influence on the absorption of the nickel ion at higher concentration, but it does exert some sort of influence on the absorption of nickel ions at high dilutions.

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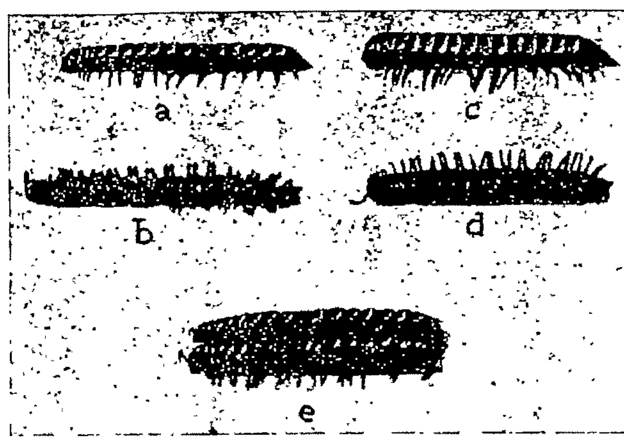
CHEMICAL EXAMINATION OF *STREPTOGONOPUS PHIPSONI* (MILLIPEDES). PART I

By Rafat Husain Siddiqui, Syed Khader Basha and Syed Maqsud Ali

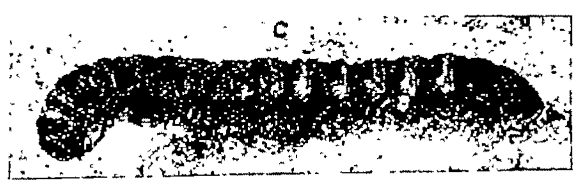
Streptogonopus phipsoni (Millipedes) belongs to the family of *Strongy Losomodæ*. The worms are generally 25 mm. in length and 2·6-3 mm. in width in the case of males and 3 6 mm. in the case of females. The head, trunk and legs are of a bright dark chestnut colour in adults and pinkish red in the young ones. The pink colour changes to dark brown on exposure to light. The body consists of segments which are constricted in the suture and the male has got thicker legs. They are found in the United Provinces, Bihar, Punjab, and Bombay etc. (Pocock, *J. Bombay Nat. Hist. Soc.*, 1892, **7**, 151; Attems, *Arch. Naturg.*, 1914, LXXX, A 4, p. 219) (Figs. 1 and 2).

Fig. 1.



S. Phipsoni (Losomodæ) a, b, male ; c, d, female ; e, mating

Fig. 2.



S. Phipsoni (Losomodæ) female.

During rainy season the worms attracted our attention and as no information was available they were subjected to a chemical examination. The worms come out in large numbers with rains and disappear at the close of the rainy season after producing two breeds. On keeping in *vacuo* over sulphuric acid they turn brittle but on re-exposing to air only the females come to life. They show moisture (51·4%) and in the ash (62·3% on the weight of dry animals) sodium, potassium, iron, magnesium, calcium, silica, sulphate, chloride and carbonate have been detected. On extraction with alcohol a protein is obtained showing proteinous nitrogen (52·06%) and xanthoprotein reaction and also a ruby-red to brown oil from which dimethylglyoxime has been separated. The isolation of this substance from millipedes marks the first instance where an oxime has been obtained from a living organism. As regards its occurrence there are three possibilities *viz.*, (*i*) it occurs as such, (*ii*) it is a decomposition product, (*iii*) it is a product of resynthesis. Future work will clear this point and therapeutic studies will decide its utility in medicine.

Experimental

A few hundred pairs of adult millipedes were picked and kept in a glass basin with earth and grass. It was noticed that from time to time the males were cast off dead by the females.

and they went in search of new ones. They seem to hate intense sunlight but come out in the mornings and evenings in an orderly manner to a neat place and on being touched or disturbed they move very quickly in disorder in all directions. They emit a nauseating odour and secrete a bad-smelling fluid which does not produce any irritating effect or blisters on hands. The odourous principle is volatile with steam. The pink colour of the young breed changes to dark brown on exposure to light and with age.

About two dozen mating pairs were kept in *vacuo* over sulphuric acid when the males began to separate from the females and soon all turned brittle. After 15 minutes they were taken out from the desiccator and exposed to the air. After half an hour the females began to show signs of life and within two hours 90% began to move while none of the males showed any sign of life and remained brittle.

A representative sample of hundred worms was taken and was freed of adhering earth by washing with water. The worms were dried in *vacuo* at 100° and the dried worms were converted into ash (Table I), which indicated the presence of sodium, potassium, iron, calcium, magnesium, silica, sulphate, chloride and carbonate. It is difficult to say whether these constituents form part of millipedes or are derived from the unassimilated matter of the alimentary canal. A dissection of the worms would decide this. The worms on extraction with various solvents gave the following percentages of the extractables.

TABLE I

Moisture	... 51·4%
Ash on dry worms	... 62·3
Water-soluble ash	... 11·6
Sodium in water soluble ash *	... 2·7
Potassium in water-soluble ash †	... 3·27

TABLE II

Solvent,	
Ether	... 4·05%
Acetone	... 2·7
Chloroform	... 2·58
Benzene	... 1·171
Petroleum ether	... 1·50

Extraction of worms with Alcohol.—The worms (300 g.) were washed with water and percolated with alcohol (500 c.c.) for 72 hours. They were next extracted with alcohol on the water-bath for 6 hours. The combined extracts on standing deposited a pinkish sediment which on washing with ether turned as a dull white amorphous mass (A) The alcoholic filtrate was concentrated to 100 c.c. in *vacuo* and gave no deposit on keeping at 0° and was shaken with ether (5 times). The ether solution after washing and drying over anhydrous sodium sulphate gave viscous oily liquid (B). The immiscible liquid on treatment with neutral lead acetate yielded a lead salt which after deleading in alcoholic solution gave a small quantity of a brown sticky residue.

Fraction (A) was obtained as an amorphous powder (2 g.) and was insoluble in common organic solvents. It did not melt below 300° and showed absence of sulphur, phosphorous, and gave nitrogen by Kjeldal's method (8·33%) (52·06% as protein when 6·25 was used as factor). It gave xanthoprotein reaction and decolourised 5% solution of potassium permanganate. When warmed with concentrated sulphuric acid it turned deep brown while with concentrated sulphuric acid and potassium dichromate it gave a green solution in the cold which turned deep green on warming.

* By uranyl zinc acetate method, "Organic Reagents for Metals & for Certain Acid Radicals" by the Staff of the Research Laboratory of Hopkins and Williams Ltd, 3rd. edition, 1938 (London).

† By perchlorate method, W.A. Davis, *J. Agric. Sci.*, 1912 15, 52.

Fraction (*B*) was soluble in common organic solvents and gave a positive test for nitrogen. It was extracted (10 g.) with 10% hydrochloric acid but the acid solution on neutralisation with sodium carbonate gave only a faint turbidity. The acid-insoluble fraction was extracted with 5% sodium carbonate solution. The alkaline solution on neutralisation with 10% hydrochloric acid gave olive-green precipitate which was partly soluble in ether (1·5 g., insol., 0·7 g.). The alkali-insoluble residue was taken up in ether and after washing with water was dried over anhydrous sodium sulphate. The solvent was removed and the residue on keeping at 0° deposited a crystalline mass [0·22g. 0·06% on the wt. of worms or 3·1% on the wt. of oily substance (B)]. It was soluble in alcohol, ether and acetone but insoluble in petroleum ether and crystallised from alcohol in bunches or needles, m. p. 234-35° (Fig. 3). Its solution tinged nickel spatula pink and this suggested its resemblance with dimethylglyoxime and led to its identification. It did not give any depression with an authentic sample of dimethylglyoxime, m.p. 234-35° [m.p. 234-35°, Dictionary of Applied Chemistry by Thorpe, Vol. IV, p. 6, (1940); m.p. 234, Organic Chemistry by Perkin and Kipping, Vol. III, p. 745, (1934); m.p, 245-46°, Meyer-Jacobson, I, (ii), 826, (1913)] and gave metallic complexes identical with those obtained with the synthetical samples (Table III). (Found in material dried at 100°: N, 24·08. Calc. for $C_4H_8O_2N_2$: N. 24·13 per cent).

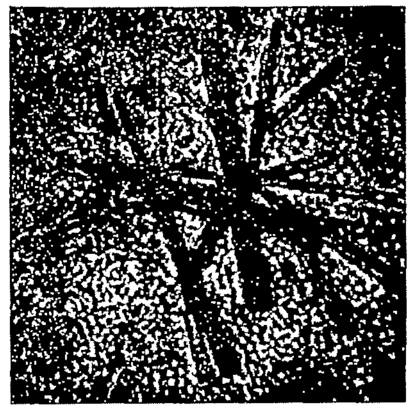


Fig. 3. Dimethylglyoxime (m p. 234-235°) (140 times mag.)

TABLE III

Metallic complexes with dimethylglyoxime

Reagents.	Dimethylglyoxime : isolated sample. 1%	5%	20%	Dimethylglyoxime: synthetic sample. 1%	5%	20%
Nickel chloride	Pink ppt.	Red ppt.	Dark red ppt.	Pink ppt.	Red ppt.	Dark red ppt.
Bismuth nitrate	Yellow ppt	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.
Ferrous sulphate	Pink soln.	Pink soln and violet ppt.	Pink soln.	Pink soln.	Pink soln. & violet ppt.	Pink soln & deep. Violet ppt.

The filtrate from dimethylglyoxime yielded a brown residue, a portion of which dissolved in hot alcohol and crystallised in needles but could not be isolated in a state of purity. Alcohol-insoluble portion was not examined.

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Received December 21, 1944.

CHEMICAL EXAMINATION OF *STREPTOGONOPUS PHIPSONI* (MILLIPEDES). PART II. SOME CHEMICAL AND PHYSICAL CONSTANTS OF THE FATTY MATTER

By RAFAT HUSAIN SIDDIQUI AND SYED MAQSUD ALI

The excellent researches of Klenk, Tsujimoto, Hilditch, Collin and others (*Z. physiol. Chem.*, 1933, **221**, 67, 259, 264 ; *J. Soc. Chem. Ind. Japan*, 1920, **23**, 41, 1099 ; *Biochem. J.*, 1937, **31**, 227 ; 1938, **32**, 681 ; 1933, **27**, 1373) on Depot fats of *Amphibia*, *Reptilia* and *Insecta* have not only elucidated the composition of the saturated and unsaturated acids of the fatty matter but have also shown the specific compositional differences that exist in the fats of aquatic and terresterial animals. Considering the vast animal life our knowledge in this domain of science even now is extremely meagre.

The millipedes attracted the attention of the authors during a rainy season when they were collected and subjected to a chemical examination and as a result of this in part I of this series indication was given of a fatty matter and of a proteinous substance. Dimethylglyoxime was identified and isolated from the ether-soluble fraction of the alcoholic extract of the worms. In September, 1943, some more worms were collected mostly from the new breed and were extracted with ether. The orange ethereal solution was washed with a little water, dried over anhydrous sodium sulphate and on removal of the solvent yielded a red oil giving the nauseating odour of the worms. The oil was kept away from light and was examined in January, 1944. The fat on titration with sodium hydroxide solution gave a high value for free acids and this may be due to its keeping for such a long time. The acetyl value was also high. The iodine value is an index of low unsaturation while the low Reichert-Meissl and Polenski values indicate a small amount of glycerides of volatile acids. The constants are given below (Table I).

TABLE I

Physical and chemical constants.

Smell ...	Peculiar nauseating odour of the worms	Iodine value	30·8 ; 31 4
Colour ...	Orange or ruby-red	Acid value	75·09
Specific gravity at 21°	0·9189	Reichert-Meissl value	1·21
Refractive index at 21°	1·46848	Polenski value	0·4
Saponification value	121·3 ; 123·6	Unsaponifiable matter	8·73

Future work will establish the nature and the composition of the saturated and unsaturated acids and also their relationship and importance with reference to the herbivorous habit of the worms.

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PHYSICAL PROPERTIES OF ISOMERIC OXIMES. PART I. MOLECULAR CONDUCTIVITIES IN LIQUID SULPHUR DIOXIDE OF ISOMERIC ALDOXIMES

By N. K. Patwardhan and S. S. Deshapande

Solutions of oximes in liquid sulphur dioxide gave measurable conductivities. The β-aldoximes in all cases gave higher conductivities than α-aldoximes. Hence by extension of Ostwald's rule regarding ethylenic acids to the aldoximes, the β-forms should be *'anti'* and the α-form, *'syn'*. These configurations are in agreement with the observations of Beckmann and Meisenheimer.

The object of this work was to seek relation, if any, between configurations and electrical conductivities of isomeric oximes. Brady and Goldstein (*J. Chem. Soc.*, 1926, 1918) observed conductivities of sodium salts of isomeric aldoximes in aqueous solutions and determined indirectly the dissociation constants K_a of aldoximes from the relations

$$\Lambda_{\text{obs}} = (1-x)\Lambda_v + x\Lambda_{\text{NaOH}} \qquad K_h = \frac{x^2}{(1-x)\,v} \qquad K_a = \frac{K_w}{K_h}$$

where Λ_{obs} is the observed conductivity of the sodium salt of an oxime at dilution v, x is the degree of hydrolysis, Λ_v is the conductivity of the unhydrolysed salt, Λ_{NaOH} is the conductivity of caustic soda and K_w, K_a and K_h are dissociation constant of water, dissociation constant of the oxime and hydrolysis constant of the sodium salt of the oxime respectively. They have shown that in every case of isomeric oximes they observed, the dissociation constant of the α* form was greater than that of the β-form.

The authors have not given the values of Λ_{obs}, but it may be assumed that these are related to K_a. They prepared solutions of sodium salts by dissolving oximes in calculated quantity of pure aqueous caustic soda.

We prepared sodium salts by adding to an alcoholic solution of an oxime, equivalent amount of sodium dissolved in alcohol and precipitating by addition of ether (Beckmann, *Ber.* 1889, **22**, 434 ; Goldschmidt and Röder, *Ber.*, 1895, **28** 2013). Conductivity measurements of the sodium salts of oximes, thus prepared, revealed that whereas in the case of benzaldoxime the sodium salt of α-form has higher conductivity than that of the β-form, opposite is the case with *m*-nitrobenzaldoxime. We felt therefore the need of direct comparison of the conductivities of oximes themselves.

On account of their very small solubility and poor ionisation in water, conductivities of oximes in aqueous solutions are inconvenient for comparison. Solutions in non-aqueous solvents like pure acetic acid and nitrobenzene gave very feeble conductivities. The oximes were, however, found to dissolve in liquid sulphur dioxide and these solutions gave measurable conductivities. However, on account of their limited solubility in this solvent and also owing to the difficulty of maintaining constant temperature (-18° in our experiments) for a long period we could vary dilutions only within a limited range.

In all cases of isomeric oximes studied we found the molecular conductivity of the β-form higher throughout than that of α-form. Owing, however, to experimental

* The terms *'syn'* and *'anti'* are avoided because the applications of these configurations to the isomeric forms is the subject of discussion.

difficulties exactly equal dilutions of the two forms could not be obtained for comparison of conductivities. But as will be clear from the tables, when the dilutions of the two forms are more or less equal, the β- form has a much higher conductivity than α-form. Such values of conductivities are shown by asterisks in the tables.

The α-forms were obtained by oximation of aldehydes in alkaline medium, while the β-forms were prepared from the correspoinding α- forms through the hydrochlorides or by exposure of the α-form in benzene solution to sunlight. In the case of cinnamic aldehyde, oximation in alkaline medium gave only the β- form and not a mixture of the α- and β-forms as described by Brady and Choksi (*J. Chem. Soc.*, 1929, 947). With furfuraldehyde in alkaline medium Brady and Goldstein (*ibid.*, 1927, 195) obtained α- aldoxime. They observed that if their conditions are not carefully followed inseparable mixture of α- and β-forms is obtained. We obtained the pure β- form instead of the α- form or the mixture. Its high molecular conductivity is in conformity with the behaviour of β- oximes (Table VI).

In the case of *p*-methoxybenzaldehyde we found that of the two α-forms described in literature, the one melting at 60° (Goldschmidt, *Ber.*, 1889, **22**, 2790) gave low values of molecular conductivity like other α-oximes, but the other melting at 48° (Westenberger, *Ber.*, 1883, **16**, 2994) behaved like β-oximes giving high values for molecular conductivities. These values were, however, lower than the corresponding values given by the true β-oxime melting at 138° (Table V).

We were unable to get α- forms of cinnamaldoxime and furfuraldoxime.

EXPERIMENTAL

The isomeric forms of oximes were purified by crystallisation from alcohol or benzene. Sulphur dioxide, prepared from copper and pure sulphuric acid and bubbled through pure sulphuric acid, was passed through a cool coil condenser and was collected in a receiver protected from atmospheric moisture and surrounded by a freezing mixture. A small conductivity cell was filled with this solvent up to 5 c.c. mark and was surrounded by freezing mixture kept in a small thermos. The temperature could be maintained at -18° without much difficulty for a period of about 40 minutes which was sufficient for taking three or four conductivity measurements at different dilutions. The cell constant was obtained by determining resistances of solutions of potassium iodide in liquid sulphur dioxide at different dilutions and from the curve plotted from values of molecular conductivities observed by Franklin for such solutions (*J. Phys. Chem.*, 1911, **15**, 675).

To minimise errors, specific conductivity of liquid sulphur dioxide was determined in each experiment and this was subtracted from the specific conductivity of solution to get specific conductivity of the solute. Different dilutions were obtained by adding small quantities of oxime to the solvent.

TABLE I

Benzaldoximes

α-Form (b. p. 104°/6 mm.)				β-Form (m.p. 128°.)			
Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. Condy $\times 10^6$	Molar condy. $\times 10^2$.	Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. condy. $\times 10^6$	Molar condy. $\times 10^2$.
0·0874 g.	6·923 c.c.	2·77	1·918	0·0368 g.	16·44 c.c.	12·97	21·33
0·1157	5·230	5·08	2·657	0·0745	8·121	16·82	13·66
0·1238	*4·889	6·00	*2·907	0·1265	*4·783	22·14	*10·59

Table II

o-Nitrobenzaldoximes

α-Form (m.p. 104°)				β-Form (m.p. 148°)			
Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. condy. $\times 10^{6}$.	Molar condy. $\times 10^{2}$	Wt of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. condy. $\times 10^{6}$.	Molar condy. $\times 10^{2}$.
0·0430 g.	19 31 c c	2·70	5 212	0·0255 g	32·56 c c.	7·037	22·91
0 0911	*9·111	5·70	*5·194	0·0556	14·93	13·80	20 60
0·0994	8·35	7·10	5·929	0 0658	12·62	18·83	23·75
...	..		...	0 0868	*9 563	24·07	*23·01

Table III

m-Nitrobenzaldoximes

α-Form (m.p. 121°)				β-Form (changes into α before melting).			
Wt. of oxime in 5 c.c	Dilution (v).	Sp. condy. $\times 10^{6}$.	Molar condy $\times 10^{2}$.	Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. condy. $\times 10^{6}$.	Molar condy. $\times 10^{2}$.
0·0661 g.	The specific conductivity is almost equal to that of the solvent itself.			0·0425 g.	19·53 c.c.	1·853	3·619
0·1291				0·1016	8·190 ,,	3·761	3·073
0 1747				0·1691	4·908 ,,	7·090	3·479

Table IV

p-Nitrobenzaldoximes

α-Form (m p. 129°)				β-Form (m.p. 182°)			
Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. condy. $\times 10^{6}$.	Molar condy $\times 10^{2}$	Wt. of oxime in 5 c c	Dilution $(v) \times 10^{-3}$.	Sp. condy $\times 10^{6}$.	Molar condy $\times 10^{2}$.
0·0098 g.	84·70 c c.	0·506	4·286	0 0140 g.	59 29 c c.	3·044	18·05
0·0236	35·18	2·630	9·251	No more of the substance could be dissolved.			

Table V

p-Methoxybenzaldoximes

α-Form (m. p. 60°)				β-Form (m. p. 138°)			
Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp condy. $\times 10^{6}$.	Molar condy. $\times 10^{2}$.	Wt of oxime in 5 c c.	Dilution $(v) \times 10^{-3}$	Sp. condy. $\times 10^{6}$.	Molar condy. $\times 10^{2}$.
0·0256 g.	*29·99 c.c.	1 299	3 832*	0·0120 g.	62·91 c.c.	4·761	29·95
0·0660	11·44	3·195	3·656	0·0286	*26·39	9·66	25·50*
0·1072	7·042	4·440	3·127	0·0440	17·16	15·45	26·51

α- Form (m. p. 48°)

0·0254	29·73	8·93	26·55
0·0592	12·76	13·70	17·47
0·0938	8·048	20·53	16·52

TABLE VI

Furfuraldoximes

β-Form (m. p. 92°)

Wt of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp. condy. $\times 10^{6}$.	Molar condy. $\times 10^{2}$.
0·0296 c.c.	18·75 c.c.	20·22	37·92
0·0986	5·628	48·81	27·48

TABLE VII

Cinnamaldoximes

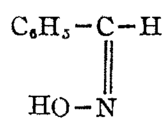
β-Form (m. p. 136°)

Wt. of oxime in 5 c.c.	Dilution $(v) \times 10^{-3}$.	Sp condy. $\times 10^{6}$.	Molar condy $\times 10^{2}$.
0·0280 g	26·25 c.c.	8·49	30·91
0·0736	9·986	13·33	7·491
0·0964	7·625	16·93	4·503

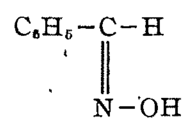
DISCUSSION

Brady and Goldschmidt (*loc. cit.*) commenting on the doubt cast upon Hantzsch's original formulation of aldoximes (*Ber.*, 1891, **24**, 13) observe :—

"On the other hand if the principle applied by Ostwald (*Z. physikal. Chem.*, 1892, **9**, 553) to the acids of ethylene series, that in an acid the proximity of a so-called 'acidic' group tends to increase the dissociation constant of the acid, can be applied to aldoximes, the benzaldoxime of the *anti*-type where the negative phenyl group is vicinal to the aldoximino hydroxyl group should have a higher dissociation constant than the *syn*-isomeride in which the two groups are further apart".



anti



syn

Since they found indirectly that the α-oximes have a higher dissociation constant, the α-forms are '*anti*' and the β-forms are '*syn*' in agreement with Hantzsch's original configuration. But since we find by direct measurements that the β-forms have a higher conductivity and, therefore, a higher dissociation constant than the α-forms, the β-forms must be '*anti*' and the α-forms '*syn*'. These configurations are reverse of those of Hantzsch's but they are in agreement with those proposed on experimental evidence by Beckmann (*Ber.*, 1923, **56**, 341) and Meisenheimer (*Annalen*, 1926, **446**, 205).

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NORMAL AND POLYMOLYBDATES OF SOME COMPLEX CATIONS AND THE COMPOSITION AND CONSTITUTION OF METAMOLYBDATES

By Priyadaranjan Rây and Byomkes Sarma

Normal and polymolybdates of some complex metal cations have been prepared and their properties studied, specially the dehydration of metamolybdates. The results have been found to support Rosenheim's scheme of formulation for the metamolybdates in preference to those advocated by Jander, Brintzinger, Keggin and others.

In a previous paper (Rây and Siddhanta, *J. Indian Chem. Soc.*, 1941, **18**, 397) the composition and constitution of paramolybdates were studied by preparing paramolybdates of a number of complex biguanide metal cations of high equivalent weight and examining their properties, specially that of dehydration. A similar study has been extended in the present paper to the metamolybdates. Incidentally some new normal and paramolybdates have also been described.

As in the case of paramolybdates different views are held regarding the composition of metamolybdates.

Rosenheim (Rosenheim and Felix, *Z. anorg. Chem.*, 1913, **79**, 292) on the basis of Werner's co-ordination theory represented metamolybdates as $R_6H_4[H_2(Mo_2O_7)_6]$ aq., where R is a univalent positive radical.

Travers and Malaparade (*Bull. Soc. Chim.*, 1926, **39**, 1406) from potentiometric titrations formulated metamolybdates as $R_2Mo_4O_{13}$, aq.

Jander and his co-workers (*Z. anorg. Chem.*, 1929, **180**, 129 ; 1930, **187**, 60 ; 1933, **211**, 49; **212**, 1; 1934, **217**, 65) from the results of ionic diffusion experiments, which were supported by those of conductometric and thermometric titrations, as well as from a study of absorption spectra, concluded that the metamolybdates should be represented by the formula, $R_3[H_3Mo_6O_{21}]$ aq., which is closely related to that of Rosenheim, as the latter is obtained by doubling the former.

Britton and German (*J. Chem. Soc.*, 1930, **128**, 2154) from potentiometric titration and Bye (*Bull. soc. chim.*, 1939, **6**, 174) from conductometric titration confirmed the formation of metamolybdates of the composition, $Na_2O, 4MoO_3$.

Brintzinger and Ratanarat (*Z. anorg. Chem.*, 1935, **224**, 97) from the measurement of the rate of electrodialysis of polymolybdate ions obtained values for the ionic weight of metamolybdates in good agreement with those of Jander.

From a consideration of co-ordination number in ionic crystals Pauling (*J. Amer. Chem. Soc.*, 1929, **51**, 1010, 2868) suggested that the metamolybdates should be represented by the formula, $H_6[H_2O_4.Mo_{12}O_{18}(OH)_{36}]$.

Keggin (*Proc. Roy. Soc.*, 1934, **144A**, 75) formulates the metamolybdates as $R_6[H_2Mo_{12}O_{40}]$ aq. from a consideration of crystal structure and the dehydration of twelve heteropolyacids.

In the present paper the dehydration of cobaltic trisbiguanide metamolybdate and triethylenediamine cobaltic metamolybdate was studied as they could be obtained in a pure state by precipitation from solution.

EXPERIMENTAL

Cobaltic trisBiguanidinium Chloromolybdate (Normal).—When a strong solution of sodium normal molybdate was added, drop by drop with stirring, to a large excess of that of cobaltic *tris*biguanidinium hydrochloride (Rây and Dutt, *J. Indian Chem. Soc.*, 1939, **16**, 621), a beautiful orange coloured crystalline product readily separated out. The crystals were washed first with ice-cold water and then with alcohol, and finally dried in air.

The product is soluble in hot water, but on recrystallisation from the latter it was found to undergo partial hydrolysis giving a mixture of chloro- and hydroxo-molybdates in the form of beautiful silky scales. Found : {N, 38·57; Cl, 6·51; Mo, 16·95; Co, 10·69.

$\left[Co\,(BigH^+)_3 \right] \begin{matrix} Cl \\ \cdot \\ MoO_4 \end{matrix}$ requires N, 37·67; Cl, 6·37; Mo, 17·21; Co, 10·58 per cent ; where BigH = one molecule of biguanide, $C_2N_5H_7$.

Cobaltic trisBiguanidinium Normal Molybdate.—Cobaltic *tris*biguanidinium hydrate (Rây and Dutt, *loc. cit.*) (2g.), dissolved in the least quantity of water, was mixed with a solution of sodium normal molybdate (1·8g.). The mixture was filtered and to the filtrate a solution of ammonium acetate (2g.) was added, drop by drop, with vigorous stirring. Reddish brown needle-shaped crystals appeared readily. These were washed first with ice-cold water and then with alcohol. The crystals were dried in air. The product is soluble in hot water. Found : {N, 31·82; Co, 8·90, 8·92; Mo, 22·04, 21·90; H_2O (by loss at 92°), 8·86. $[Co\,BigH^+)_3]_2\,(MoO_4)_3, 6{\cdot}5H_2O$ requires N, 31·79; Co, 8·90; Mo, 21·80; H_2O, 8·85 per cent}.

On recrystallisation from hot water it gave a different hydrate in the form of beautiful deep red silky crystals. Found : {N, 33·28 ; Co, 9·34; Mo, 23·01. $[Co\,(BigH^+)_3]_2\,(MoO_4)_3, 3H_2O$ requires N, 33·38; Co, 9·38; Mo, 22·89 per cent}.

Nickel Biguanidinium Normal Molybdate.—A solution of nickel biguanidinium chloride (Rây and Purakayastha, *J. Indian Chem. Soc.*, 1941, **18**, 217) was added with stirring to that of sodium molybdate. Beautiful yellowish brown crystals of the product separated from the solution. These were washed and dried as usual. Found : {N, 29·53; Ni, 12·39; Mo, 20·37. $[Ni\,(BigH^+)_2]\,MoO_4, 3H_2O$ requires N, 29·49; Ni, 12·37; Mo, 20·22 per cent}.

Copper Biguanidinium Normal Molybdate.—The substance was obtained as a beautiful violet crystalline precipitate by mixing a solution of copper biguanide chloride (Rây and Bagchi, *J. Indian Chem. Soc.*, 1939, **16**, 617) with that of sodium normal molybdate. The crystals were washed and dried as before. Found : {N, 29·66 ; Cu, 13·49 ; Mo, 21·01. $[Cu\,(BigH^+)_2]\,MoO_4, 2{\cdot}5H_2O$ requires N, 29·75; Cu, 13·42; Mo, 20·40 per cent}.

Preparation of the complex metamolybdates presented some difficulties. Interaction of sodium metamolybdate with cobaltic *tris*biguanidinium chloride in aqueous solution led to products of indefinite composition with a ratio of Co : Mo approximately equal to 1 : 2, in place of 1:6 as required for the metamolybdate. This seems to suggest that sodium metamolybdate in aqueous solution suffers partial hydrolysis with formation of lower molybdates. Digestion of the solid cobaltic *tris*biguanidinium normal molybdate in a buffer solution of p_H 2 also did

not give the desired product, though the range of stability of metamolybdates in aqueous solution lies between p_H 1·5 and 2·9. Even when a solution of the cobaltic *tris*biguanidinium normal molybdate was substituted for the solid, no better results were obtained. The pure complex paramolybdate could, however, be obtained in this way by using a buffer solution of p_H 4 (approximately). The range of stability of the paramolybdates in solution lies between p_H 3 and 4·5.

Cobaltic tris*Biguanidinium Paramolybdate.*— Cobaltic *tris*biguanidinium normal molybdate (2g.) was dissolved in 50 c.c. of water on the water-bath. The solution was filtered and added, drop by drop with stirring, to that of a buffer solution of p_H 4, made by mixing 200 c.c. acetic acid (0·2*N*) and 50 c.c. of sodium acetate solution (0·2*N*). The mixture was then heated on the water-bath for 10-15 minutes. The dull red crystalline precipitate was washed and dried as usual. Found {N, 21·56 ; Co, 6·21, 6·10 ; Mo, 34·50, 34·53.
$[Co(BigH^+)_3]_2(Mo_7O_{24})$, $9H_2O$ requires N, 21·64; Co. 6·07; Mo, 34·61 per cent}.

Prepared in a different way this compound has already been described by Rây and Siddhanta (*loc. cit.*).

Pure complex metamolybdate was finally obtained from a nitric acid solution of p_H 2·5 (approximately) in which cobaltic *tris*biguanidinium nitrate and sodium metamolybdate were made to react.

Cobaltic tris*Biguanidinium Metamolybdate.*—Light yellow crystals of sodium metamolybdate were obtained by allowing an acid solution of sodium normal molybdate (1g. $Na_2MoO_4, 2H_2O$ dissolved in 6·2 c.c. of *N*-HCl) to evaporate in air at the room temperature for about 10-15 days. The crystals were washed first with ice-coid water and then with alcohol. They were dried in air. Found : {Na, 6·31; Mo, 52·26, 52·12. $Na_2O.4MoO_3$, $5H_2O$ requires Na, 6·32; Mo, 52·74 per cent}.

Cobaltic *tris*biguanidinium nitrate (1g.), (Rây and Dutt, *loc. cit.*) was dissolved in the least quantity of nitric acid of p_H 2·5 (approx.) in the cold. This was then added, drop by drop with stirring, to a solution of sodium metamolybdate (2g.) in the same solvent. A beautiful pale violet precipitate appeared. The mixture was set aside to settle. The precipitate was filtered, washed free of nitric acid first with ice-cold water and then with alcohol. The product was dried in air. The substance is insoluble in water and dilute acids. Found : {N, 15·07; Co, 4·24, 4·26 ; Mo, 40·96, 41·48 ; H_2O (by loss at 100°), 7·98.
$[Co(BigH^+)_3]_2(H_8Mo_{12}O_{42})$, $12·5H_2O$ requires N,15·11; Co,4·25; Mo,41·45; H_2O, 8·06 per cent}.

Dehydration

Substance taken = 0·8804g.

Temp.		60°	70°	80°	90°	100°	110°
Loss of water in g.		0 0510	0·0608	0·0628	0·0654	0·0699	0·0699
,,	in %	5·79	6·91	7·13	7·42	7·98	7·98
,,	in moles	8·94	10·60	11·0	11·44	12·32	12.32

The product dehydrated at 100° gave on analysis: Co, 4·64; Mo, 45·28.
$[Co(BigH^+)_3]_2[H_8Mo_{12}O_{42}]$ requires Co, 4·61 ; Mo, 45·0 per cent. The dehydrated substance regained its original weight after a few days, on exposure to atmospheric air at the room temperature.

TrisEthylenediamine Cobaltic Metamolybdate.—A solution of sodium metamolybdate (1 g.) in dilute nitric acid (p_H = 2·5 approx.) was added drop by drop to that of *tris*ethylenediamine cobaltic chloride trihydrate (1 g.) in the same solvent. A pale yellow flocculent precipitate separated from the solution. The product was allowed to settle, washed free of hydrochloric acid with ice-cold water and alcohol. It was then dried in air. {Found : N, 6·58 ; Co, 4·72, 4·64 ; Mo, 45·0, 45·28 ; H_2O (by loss at 100°), 9·59. $[Co\,En_3]_2[H_6Mo_{12}O_{42}]$, $13·5H_2O$ requires, N, 6·59; Co, 4·63 ; Mo, 45·16 ; H_2O, 9·52 per cent}, where En=one molecule of ethylenediamine, $C_2N_2H_8$.

Dehydration.

Substance taken=0·5632 g.

Temp.	60°	70°	80°	90°	100°	110°
Loss of water in g	0·0369	0·0455	0·0496	0·0520	0·0540	0·0540
,, %	6·550	8·078	8·806	9·237	9·590	9·590
,, moles	9·30	11·50	12·56	13·06	13·56	13·56

The product dried at 100° gave on analysis : Co, 5·15 ; Mo, 49·79. $[Co.\,En_3]_2[H_6Mo_{12}O_{42}]$ requires Co, 5·11 ; Mo, 49·90 per cent.

The dried substance regained its original weight on exposure to air for several days at the room temperature.

Another product on analysis gave : N, 6·71; Co, 4·66, 4·75; Mo, 45·45, 45·36 ; H_2O (by loss at 100°) 8·26. $[Co.En_3]_2$-$[H_6Mo_{12}O_{42}]$, $11·5H_2O$ requires N, 6·68 ; Co, 4·69; Mo, 45·81 ; H_2O, 8·19 per cent}.

Dehydration.

Substance=0·8035 g.

Temp.	60°	70°	80°	90°	100°	110°
Loss of water in g	0·0483	0·0569	0·0589	0·0622	0·0652	0·0664
%	6·01	7·08	7·33	7·74	8·12	8·26
moles	8·44	9·95	10·30	10·89	11·40	11·62

The product thus dehydrated gave on analysis: Co, 5·15; Mo, 49·79. $[Co.En_3]_2\,[H_6Mo_{12}O_{42}]$ requires Co, 5·11 ; Mo, 49·90 per cent.

DISCUSSION

The results of dehydration experiments on the complex metamolybdates, summarised in Table I, show that the metamolybdates contain three molecules of bound or constitutional water.

TABLE I

Substance.	Loss of water in moles at 60°	70°	80°	90°	100°	110°	Gain of water in moles when exposed to air.
Cobaltic *tris*biguanidinium metamolybdate $[Co(BigH^+)_3]_2\,Mo_{12}O_{39}$, $15·5H_2O$	8·94	10·60	11·0	11·44	12·32	12·32	12·30
Cobaltic *tris*ethylenediamine metamolybdate $[Co.En_3]_2\,Mo_{12}O_{39}$, $16·5H_2O$	9·30	11·50	12·56	13·06	13·56	13·56	13·50
,, ,, $14·5H_2O$	8·44	9·95	10·30	10·89	11·40	11·62	11·50

In Table II the composition of these metamolybdates are represented by formulae based on different views and their crystal water content compared with the experimentally determined values.

TABLE II

Substance.	Formula	Crystal water calc.	Crystal water found
1. Cobaltic *tris*-biguanidinium metamolybdate	$[Co(BigH^+)_3]_2Mo_{12}O_{39}$, $15{\cdot}5H_2O$ (older formula)	10·04%	7·95%
	$[Co(BigH^+)_3]_2H_4[H_2(Mo_2O_7)_6]$, $12{\cdot}5H_2O$ (Rosenheim)	8·06	
	$[Co(BigH^+)_3][H_3Mo_6O_{21}]$, $6{\cdot}25H_2O$ (Jander)	8·06	
	$[Co(BigH^+)_3]_2[H_2Mo_{12}O_{40}]$, $14{\cdot}5H_2O$ (Keggin)	9·39	
2. Cobaltic *tris*-ethylenediamine metamolybdate	$[Co.En_3]_2Mo_{12}O_{39}$, $16{\cdot}5(14{\cdot}5)H_2O$ (older formula)	11·64 (10·38)	9·59% (8·26)%
	$[Co.En_3]_2H_4[H_2(Mo_2O_7)_6]$, $13{\cdot}5(11{\cdot}5)H_2O$ (Rosenheim)	9·52 (8·23)	
	$[Co.En_3][H_3Mo_6O_{21}]$, $6{\cdot}75(5{\cdot}75)H_2O$ (Jander)	9·52 (8·23)	
	$[Co.En_3]_2[H_2Mo_{12}O_{40}]$, $15{\cdot}5(13{\cdot}5)H_2O$ (Keggin)	10·93 (9·66)	

In Table III the results of analysis of the dehydrated products are summarised for comparison with those required for the different formulae.

TABLE III

Substance.	Formula.	Found Co.	Found Mo.	Calc. Co.	Calc. Mo.
1. Cobaltic *tris*biguanidinium metamolybdate	$[Co(BigH^+)_3]_2Mo_{12}O_{39}$ (older formula)	4·72%	46·08%	4·64%	45·28%
	$[Co(BigH^+)_3]_2[H_6Mo_{12}O_{42}]$ (Rosenheim)	4·62	45·11		
	$[Co(BigH^+)_3][H_3Mo_6O_{21}]$ (Jander)	4·62	45·11		
	$[Co(BigH^+)_3]_2[H_2Mo_{12}O_{40}]$ (Keggin)	4·69	45·75		
2. Cobaltic *tris*ethylenediamine metamolybdate	$[Co.En_3]_2Mo_{12}O_{39}$ (older formula)	5·24	51·11	5·15	49·79
	$[Co.En_3]_2[H_6Mo_{12}O_{42}]$ (Rosenheim)	5·11	49·91		
	$[Co.En_3][H_3Mo_6O_{21}]$ (Jander)	5·11	49·91		
	$[Co.En_3]_2[H_2Mo_{12}O_{40}]$ (Keggin)	5·19	50·70		

From an examination of these tables it will be clear that the experimental results support the scheme of formulation advocated by Rosenheim or Jander. But as it has been found by X-ray study that a six-fold aggregation cannot represent the metamolybdate, preference should be given to Rosenheim's formula. At the same time it must, however, be pointed out that this cannot altogether exclude Keggin's formulation as it is sometimes found that last one or two molecules of water of hydration in the case of some salts cannot be removed even when dried at or about 110°.

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SUPERSATURATION LIMITS OF SOLUTIONS. PART III.

By Rama Gopal and A. C. Chatterji

It has been shown that the equation of Jones and Partington and hence the equation $\lambda_0(T_s - T) = 2M\sigma T_s/\rho r$ derived therefrom is applicable to supersaturated solutions of electrolytes and that the values of the heats of solution at ordinary temperatures, instead of those at the absolute zero, may be employed for approximate calculations.

Jones and Partington (*Phil. Mag.*, 1915, **29**, 35) have shown that equation (1) rests on the consideration of

$$T = C\left(1 - \frac{2M\sigma}{\rho\lambda_0 r}\right)$$

$$= T_s\left(1 - \frac{2M\sigma}{\rho\lambda_0 r}\right) \qquad \ldots \quad (1)$$

the Ostwald-Freundlich equation (1, *a*) (*Z. physikal. Chem.*, 1909, **34**, 497; Freundlich, "Kapillarchemie," 1909, p. 144), which is applicable to dilute solutions of non-electrolytes.

$$\frac{RT}{M} ln\frac{S_2}{S_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad \ldots \quad (1, a)$$

(The terms in the above equations have their usual significance). Hence the use of the equation,

$$\lambda_0(T_s - T) = \frac{2M\sigma}{\rho r} T_s \qquad \ldots \quad (2)$$

which is based on equation (1) (*cf. J. Indian Chem. Soc.*, 1943, **20**, 183), in the aqueous solutions of electrolytes appears at the first sight to be quite unjustified. Besides, λ_0 in (1) is the heat of solution at the absolute zero and therefore the substitution of the values of the heats of solution at ordinary temperatures for λ_0 in (2) may be a matter of serious objections. These two points were not fully discussed before due to the fact that the authors of the theory itself applied equation (1) to solutions of Glauber's salt (*loc. cit.*). However, the applicability of equations (1) and (2) to solutions of electrolytes and the use of the ordinary heats of solution λ_0 appear to be justified from the following considerations.

Ostwald-Freundlich equation can be reduced to the form

$$\frac{RT}{M} ln\frac{S}{S_\infty} = \frac{2\sigma}{\rho r} \qquad \ldots \quad (3)$$

where S denotes the solubility, of particles of radius r and S_∞, the solubitity of those of radius ∞, *i.e.*, the ordinary solubility. Jones (*Z. physikal. Chem.*, 1913, **82**, 448) has shown that for electrolytes the general Ostwald-Freundlich equation becomes:

$$\frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) = \frac{RT}{M}\left[ln(n-1)(a_1 - a_2) - \frac{n}{m-1} ln\frac{1-a_1}{1-a_2} + \frac{m}{m-1} ln\frac{a_1}{a_2}\right]$$

where a_1 and a_2 are the degrees of dissociation at concentrations S_1 and S_2, n, the number of ions per molecule of the electrolyte in question and m, the constant of the Storch's equation namely,

$$\frac{1-a}{v} = k\left(\frac{a}{v}\right)^m.$$

However, assuming the degree of dissociation * α to be constant within a small range of concentrations, a simpler equation of Mack and Dundon (*J. Amer. Chem. Soc.*, 1923, **45**, 2479) namely,

$$(1-\alpha+n\alpha)ln\frac{S_2}{S_1}=\frac{2M\sigma}{\rho RT}\left(\frac{1}{r_2}-\frac{1}{r_1}\right)$$

can be employed without undue loss of accuracy instead of the rigorous equation of Jones. Hence equation (3) becomes

$$(1-\alpha+n\alpha)ln\frac{S}{S_\infty}=\frac{2M\sigma}{\rho rRT} \quad \ldots \quad (4)$$

Equation (4) can be written as

$$i\ ln\ S=\frac{2M\sigma}{\rho rRT}+i\ ln\ S_\infty$$

or

$$ln\ S=\frac{2M\sigma}{i\rho rRT}+ln\ S_\infty \quad \ldots \quad (5)$$

where i denotes $(1-\alpha+n\alpha)$. For $ln\ S_\infty$ one must now substitute the expression $-\frac{\lambda_0}{iRT}+\frac{a'}{iR}ln\ T+C'$ instead of the expression $-\frac{\lambda_0}{RT}+\frac{a}{R}ln\ T+C$ as the latter expression holds only for undissociated substances (Hardman and Partington, *J. Chem. Soc.*, 1911, **99**, 1771). In these expressions a, a', C and C' are constants. Considering the heat of solution to be constant within a small range of concentrations and temperatures the above expression can be further reduced to $-\frac{\lambda}{iRT}+C'$ by directly integrating the equation $\frac{dlnS}{dT}=\frac{\lambda}{RT^2}$ where λ denotes the heat of solution at temperatures in the neighbourhood of T. Hence at temperature T equation (5) simplifies to

$$lnS_T=\frac{2M\sigma}{i\rho RrT}-\frac{\lambda}{iRT}+C'$$

or

$$S_T=A\ \exp.\left[\frac{2M\sigma}{i\rho RrT}-\frac{\lambda}{iRT}+C'\right] \quad \ldots \quad (6)$$

* Activities may be used instead of concentrations (*cf.* Partington, *J. Phys. Chem.*, 1932, **36**, 1853; Kolthoff, *ibid.*, 457). In this case, assuming strong electrolytes to be completely dissociated at all concentrations, the equation of Mack and Dundon becomes

$$n\ ln\frac{S_2\gamma_2}{S_1\gamma_1}=\frac{2M\sigma}{\rho RT}\left(\frac{1}{r_2}-\frac{1}{r_1}\right)$$

where γ_1 an γ_2 are the mean activity coefficients at the two concentrations. Now equation (4) given above will take the form

$$n\ ln\frac{S\gamma}{S_\infty\gamma_\infty}=\frac{2M\sigma}{\rho RT} \quad \ldots \quad (4')$$

Now assuming γ and γ_∞ to be nearly the same, as activities do not change very rapidly with concentration, (4') simplifies to

$$n\ ln\frac{S}{S_\infty}=\frac{2M\sigma}{\rho RT}$$

The rest is simple.

Similarly at $T+\partial T$, $S_{T+\delta T}=A \exp.\left[\frac{2M(\sigma+\partial\sigma)}{iR(\rho+\partial\rho)(r+\partial r)(T+\partial T)}-\frac{\lambda}{iR(T+\partial T)}+C'\right]$ ... (7)

But
$$S_T=S_{(T+\delta T)}.$$

Consequently
$$\frac{2M\sigma}{iR r\rho T}-\frac{\lambda}{iRT}+C'=\frac{2M(\sigma+\partial\sigma)}{iR(\rho+\partial\rho)(r+\partial r)(T+\partial T)}-\frac{\lambda}{iR(T+\partial T)}+C'$$

or
$$\frac{2M\sigma}{\rho r T}-\frac{\lambda}{T}=\frac{2M(\sigma+\partial\sigma)}{(\rho+\partial\rho)(r+\partial r)(T+\partial T)}-\frac{\lambda}{(T+\partial T)} \qquad \dots (8)$$

Thus the factor i completely vanishes and also λ now denotes the heat of solution at ordinary temperatures. Further simplification of (8) and neglecting of the terms involving infinitesimals of higher orders leads to the equation

$$\left(\frac{1}{T}-\frac{\rho r\lambda}{2M\sigma T}\right)\partial T=\frac{\partial\sigma}{\sigma}-\frac{\partial\rho}{\rho}-\frac{\partial r}{r} \qquad \dots (9)$$

But
$$\frac{\partial\sigma}{\sigma}-\frac{\partial\rho}{\rho}=0 \quad \text{(approx.)}$$

Therefore
$$\left(\frac{\rho r\lambda}{2M\sigma T}-\frac{1}{T}\right)\delta T=\frac{\partial r}{r} \qquad \dots (10)$$

which on integration gives
$$T=C\left(1-\frac{1}{kr}\right) \qquad \dots (11)$$

where
$$k=\frac{\rho\lambda}{2M\sigma} \text{ and } C \text{ is a constant.}$$

If T equals the saturation temperature T_s, $r=\infty$. Hence $C=T_s$. Therefore (11) can be written as

$$T=T_s\left(1-\frac{1}{kr}\right)$$

which is exactly the relationship obtained by Jones and Partington, λ now being the heat of solution at ordinary temperatures. From the last equation it is easy to obtain

$$\lambda(T_s-T)=\frac{2M\sigma}{\rho r}T_s \qquad \dots (12)$$

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OXALATO-MOLYBDATES OF SOME COMPLEX METALLIC CATIONS

By Byomkes Sarma and Priyadaranjan Rây

The reaction between acid ammonium mono-oxalatomolybdate and complex cobalt cations in aqueous solution gave products of the general formula, $R_x(NH_4)_y$ $[MoO_3(C_2O_4)]_z.xH_2O$, where R is a complex cation like $[Co(BigH^+)_3]^{3+}$, $[Co.En_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, BigH$=C_2N_5H_7$, one molecule of biguanide; En$=C_2N_2H_8$, one molecule of ethylenediamine; x, y, and z are certain specified integral numbers. In the case of cobaltic *tris*biguanide compound $y=0$, and hence only one type (normal) of salt was obtained. The composition and dehydration of these compounds furnish evidences regarding the stability of the anionic complex mono-oxalatomolybdate in aqueous solution.

The complex oxalatomolybdates of some simple metallic cations and organic bases, as well as the free complex acids in certain cases, have been studied by different workers (Pechard, *Compt. rend.*, 1889, **108**, 1052; Rosenheim, *Z. anorg. Chem.*, 1893, **4**, 352, 362; 1896, **11**, 228; *Ber.*, 1893, **26**, 1192; Rosenheim and Bertheim, *Z. anorg. Chem.*, 1903, **34**, 427, 436; Rosenheim and Weinheber, *ibid.*, 1911, **69**, 263; Spittle and Wardlaw, *J. Chem. Soc.*, 1931, 1748).

The oxalato-molybdates have been found to belong to three classes represented by

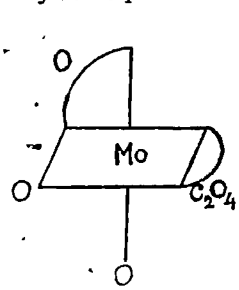
I. $R_2(RH)[MoO_3(C_2O_4)]$ aq., or $R_2(RH)[MoO_3(C_2O_4).H_2O]$ aq.

II. $R_2[(MoO_3)_2.C_2O_4]$ aq. III. $B_2[MoO_2(C_2O_4)_3]$ aq.

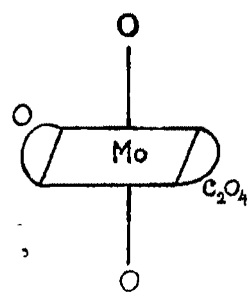
where R=H or any univalent cation and B=an organic base. Their constitution have been discussed by Rosenheim and his co-workers as well as by Spittle and Wardlaw.

In the present paper some complex cobaltammine mono-oxalatomolybdates have been described. Their composition supports the view that the molybdic and oxalic acids combine to form a complex anionic entity with hexa-co-ordinated and sexivalent molybdenum as the central atom and that this complex anion is also stable in solution. Otherwise, the sparingly soluble oxalate of the complex cations would have been precipitated from the solution along with some polymolybdates. With cobaltic *tris*biguanide chloride it gave only the normal salt, while with ethylenediamine cobaltic chloride and hexammine cobaltic nitrate it gave double ammonium salts with variable ammonia content. Some of these compounds lost all their water-content at about 80° and even the acid ammonium mono-oxalatomolybdate prepared by us contained only 1/2 mol. of H_2O, showing that this complex anion should be represented as $[(MoO_3(C_2O_4)]''$ and not as an aquo-mono-oxalatomolybdate, $[H_2O.\ MoO_3(C_2O_4)]''$ formulated by some previous workers.

Two of the three oxygen atoms in this complex anion, therefore, occupy one co-ordination position each in an octahedral configuration with the possibility for the complex to exist in *cis* and *trans* isomeric forms as shown below. Of these again the *cis*-form will be resolvable into its optical antipodes.



Cis.



Trans.

Experimental

Acid Ammonium Mono-oxalatomolybdate.—The substance was prepared according to Rosenheim's method. It gave on analysis the following results :

{Found: Mo, 36·88; C_2O_4, 33·70. $(NH_4)H[MoO_3(C_2O_4)]$, $0·5H_2O$ requires Mo, 36·92; C_2O_4, 33·85 per cent}.

Cobaltic tris*Biguanidinium Mono-oxalatomolybdate*.—A concentrated solution of acid ammonium mono-oxaltomolybdate (1g.) was added, drop by drop with stirring, to a solution of cobaltic *tris*biguanide chloride (2g.). A reddish brown precipitate separated out. The product was filtered, washed free from chloride with ice-cold water and then with alcohol. It was finally dried in air. {Found: N, 27·87; Co, 7·86; Mo, 19·22; C_2O_4, 17·52. $[Co(BigH^+)_3]_2[MoO_3(C_2O_4)]_3$, $4H_2O$ requires N, 28·15; Co, 7·91; Mo, 19·30; C_2O_4, 17·68 per cent}.

A second sample on analysis gave N, 27·67; Co, 7·66; Mo, 19·03; C_2O_4, 17·40; H_2O (by loss at 80°), 7·20. $[Co(BigH^+)_3]_2[MoO_3(C_2O_4)]_3$, $6H_2O$ requires N, 27·48; Co, 7·72; Mo, 18·84; C_2O_4, 17·28; H_2O, 7·07 per cent.

Hexammine Cobaltic Ammonium Mono-oxalatomolybdate.—(*a*) A solution of acid ammonium mono-oxalatomolybdate (<1 mol.) in water was added, drop by drop with constant stirring, to that of an excess of hexammine cobaltic nitrate (> 2/3 mol.). A yellowish brown precipitate appeared at once. This was allowed to settle, and then washed and dried as above.

{Found: N, 14·83; Co, 8·85; Mo, 28·91; C_2O_4, 26·06; H_2O (by loss at 80°) 4·05. $[Co(NH_3)_6](NH_4)[MoO_3(C_2O_4)]_2$, $1{\cdot}5H_2O$ requires N, 14·62; Co, 8·81; Mo, 28·65; C_2O_4, 26·26; H_2O, 4·03 per cent}.

(*b*) When, however, a solution of hexammine cobaltic nitrate (1g.) in water was added, drop by drop with stirring, to a solution of an excess of ammonium acid mono-oxalatomolybdate (2g.) a light yellow precipitate of different composition was obtained. This was washed and dried as usual. {Found: N, 12·55; Co, 5·84; Mo, 28·89; C_2O_4, 26·27; H_2O (by loss at 110°) 8·68. $[Co(NH_3)_6]\cdot(NH_4)_3[MoO_3(C_2O_4)]_3$, $5H_2O$ requires N, 12·59; Co, 5·90; Mo, 28·77; C_2O_4, 26·37; H_2O, 8·99 per cent}.

tris*Ethylenediamine Cobaltic Ammonium Mono-oxalatomolybdate*.—(*a*) A pale yellow crystalline precipitate was obtained from a concentrated solution of acid ammonium mono-oxalatomolybdate (1g.) and an excess of a dilute solution of *tris*ethylenediamine cobaltic chloride (1·1 g.) as described in the previous preparations. {Found: N, 12·34; Co, 6·76; Mo, 25·28; C_2O_4, 23·0; H_2O (by loss at 80°), 8·16. $[Co.\ En_3]_3(NH_4)_5[MoO_3(C_2O_4)]_7$, $12H_2O$ requires N, 12·17; Co, 6·69; Mo, 25·39; C_2O_4, 23·28; H_2O, 8·16 per cent}.

(*b*) A compound of different composition was obtained when a concentrated solution of *tris*ethylenediamine cobaltic chloride (1g.) was added to that of an ammonium hydrogen mono-oxalatomolybdate in excess (2 g.). The substance forms pale yellow beautiful crystals, sparingly soluble in water. {Found: N, 12·34; Co, 6·19; Mo, 27·40; C_2O_4, 24·60. $[Co.\ En_3]_3(NH_4)_7[MoO_3(C_2O_4)]_8$, $9H_2O$ requires N, 12·23; Co, 6·19; Mo, 26·84; C_2O_4, 24·66 per cent}.

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ESTIMATION OF CHLORIDES IN OIL-WELL DRILLING MUDS*

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The estimation by potentiometric titration of chlorine-ion concentration which has certain practical applications of importance, has been studied from the viewpoints of accuracy and reproducibility. One hundred estimations each were made of the salinity of a number of normal drilling muds whose salinities were known. The arithmetic mean of each one hundred estimations agreed closely with the calculated chloride concentrations, the maximum variation being within 0·8%. The standard deviation from the arithmetic mean did not exceed 0·72% while the most probable value (obtained graphically) corresponded within 0·1% with the arithmetic mean.

Measurement of the chlorine ion concentration of drilling muds by titration of the pressure filtrate or centrifugate with standard silver nitrate solution, using potassium chromate as indicator, was found to give results on the average 13·5% lower than the calculated values. It is thought that this may be due to the adsorption of chlorine ion on the clay particles as a result of which some of the chlorine ions present in the mud do not pass into the pressure filtrate or centrifugate.

A series of samples from two drilling wells was analysed to find if variations in the chloride content would indicate reliably when and at what depth a watersand was penetrated. Results for one well are compared with estimations of salinity of cuttings removed from the drilling mud. Variations are more distinct in the case of the results for cuttings but the two curves obtained show points of resemblance and it is concluded that if the salinity of the watersand be high enough it can be reliably detected by continuous sampling of both the ingoing and outcoming mud and estimation of the chloride content by potentiometric titration.

The reproducibility of the potentiometric titration method using silver-silver chloride electrode for the quantitative estimation of chlorides in electrolytic solutions is well known (Kolthoff and Furman, "Potentiometric Titrations", John Wiley and Sons N. Y. 1931). This method has also been used for estimating chloride content of soils (Wright "Soil Analysis", Thomas Murray & Co. London, 1943, 1st Ed., pp. 182-185.) In the estimation of the salinity of muds such as are used in oil-wells the degree of reproducibility obtainable is less certain and further, there are several sources of error, *e.g.*, poisoning of the electrode, adsorption of chlorine ion by clay particles etc. which must be guarded against. The adsorption of chlorine ion by clay particles is reduced by carrying out the titrations at a sufficiently low p_H (Snyder, *Soil. Sci.*, 1933, **35**, 43). To what extent, if at all, electrode poisoning by any particular drilling mud takes place can be ascertained only by actual titration of the mud to which known quantities of some chloride have been added. Such measurements have been made with five different samples of oil-well drilling muds.

The superiority of the electrometric method over volumetric methods for estimating chlorine ion concentration of electrolytic solutions appears well established, but its validity remains to be demonstrated in the case of muds or soil suspensions. Investigations on this topic have been carried out using both the filtrate obtained from the mud under pressure and the centrifugate in a series of volumetric titrations. The indicator used was potassium chromate. Samples of mud returns from two wells, and cuttings removed from the mud in one of these were examined for chloride to determine if watersands encountered in drilling could be detected by salinity changes in the drilling mud, by examination of cuttings, or by both.

Experimental

Muds.—Five different samples of mud were used, characteristics of which are indicated in Table I. The first was a mixture of raw clay and water and the second a mud of

* Contribution from the Research Laboratories of the Burmah Oil Company.

similar composition which had been treated with chemicals to improve its properties. The third was typical of well-matured drilling mud, while the fourth was a mud which had suffered contamination in several respects in course of use. The fifth was a sample of a typical drilling mud taken at a well.

TABLE I

Characteristics of mud used

No.	Method of preparation.	solids%.	p_H.	Initial salinity (parts/100,000).
1	Raw clay + water	33·7	7·22	5·5
2	Raw clay + water with subsequent chemical treatment	33·8	7·96	12·3
3	Reconditioned field mud	19·9	10·12	9·3
4	Well mud returns (unreconditioned)	35·5	9·71	20·0
5	Typical well mud	22·8	9·20	1·5

Reagents and Apparatus.—The strength of the pure silver nitrate solution used for titration was 0·00854N. The same silver nitrate solution was used for both volumetric and potentiometric titrations.

The apparatus for potentiometric measurements was more or less the same as that used by R. J. Best (*J. Agric. Sci.*, 1929, **19**, 533) for analysis of soils. A silver-silver chloride electrode was connected by means of a saturated potassium nitrate bridge containing 3% agar agar with a quinhydrone electrode, consisting of a platinum foil dipped in a buffer solution of p_H 3·0. The silver-silver chloride electrode was immersed in the mud wich was titrated with a 0·00854N silver nitrate solution, until the direction of the current as indicated by a pointer galvanometer (1 scale division$=10^{-7}$ amp.) was just reversed. The galvanometer connected the two half-cells through a taping key. The reversal of the current took place within 0·05 c.c. of the silver nitrate solution.

The silver-silver chloride electrode was prepared by sealing a piece of silver wire 1 mm. in diameter into a piece of glass tubing. The wire was coated over a length of about 3 cm. with silver chloride by making it the anode in the electrolysis of $N/10$-sodium chloride solution.

The quinhydrone electrode was prepared by adding 0·05 g. of quinhydrone to 12 c.c. of buffer solution of p_H 3·0 in a small beaker of 25 c.c. capacity.

Method.—The mud (5 c.c.) was diluted to 50 c.c. with distilled water in a 100 c.c. beaker and made acidic with sulphuric acid till the p_H was about 2·0. The silver—silver chloride electrode and the agar-bridge reached nearly to the bottom of the beaker and the suspension was stirred from time to time with a glass rod. The titration was continued until the galvanometer deflection was just reversed. About fifteen minutes were required for each electrometric titration.

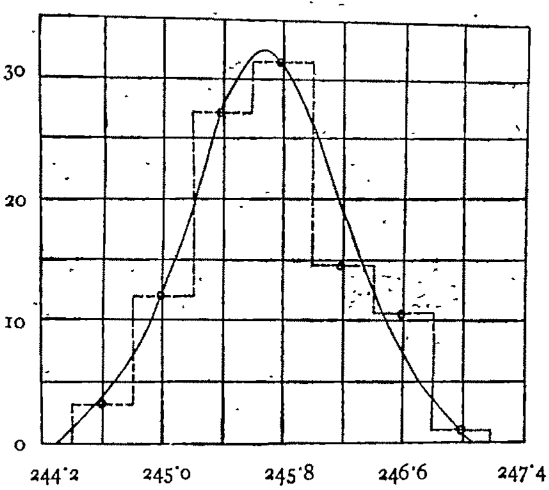
RESULTS AND DISCUSSION

Known volumes of mud No. 3 were treated with various quantities of normal sodium chloride solution and the chloride content of each sample separately estimated by the electrometric method. The results are shown in Table II. The maximum deviation of observed salinity from the calculated value did not exceed 2% and the average deviation was $-0·44$%.

Thus the electrometric method is liable to give results 0·44% too low. This deviation is probably due to slight adsorption or blanketing of chlorine ion by clay particles of the gel. The difference is, however, within the range of experimental error.

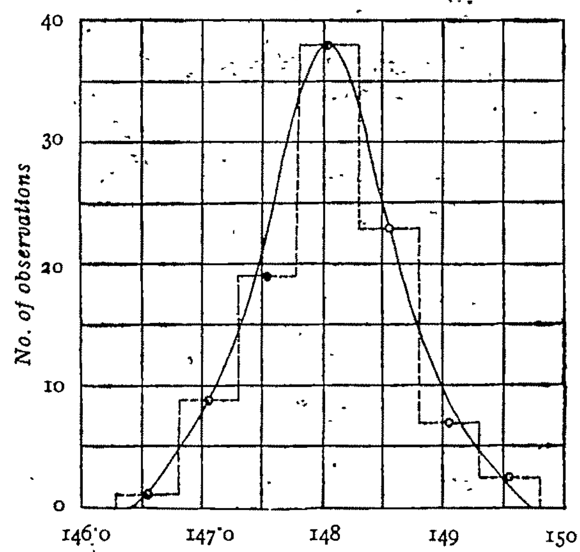
In order to test the reproducibility of this method several mud samples of known salinity were prepared from all the five mud samples mentioned in Table I. One hundred separate salinity estimations were made with each sample prepared from muds Nos. 1, 2, 4 and 5. Some of the results are shown in Figs. 1 and 2.

FIG. 1



Observed salinity (parts/100,000).

FIG. 2



Observed salinity (parts/100,000)

The curves shown in Figs. 1 and 2 are symmetrical, resembling the normal curve of error. The most probable values in all cases closely agree with the arithmetic means. This will be clear from Table III where the standard deviations of the arithmetic means and the estimated errors of the standard deviations have been tabulated.

TABLE II

Electrometric Titration of Mud No. 3 treated with various quantities of Sodium Chloride.

Sodium chloride (N) added to 500 c.c. of mud.	Salinity calc. (Parts/100,000).	Salinity obs. (Parts/100,000).	Deviation of salinity obs. from calc. value.	Sodium chloride (N) added to 500 c.c. of mud.	Salinity calc. (Parts/100,000).	Salinity obs. (Parts/100,000).	Deviation of salinity obs. from calc. value.	Sodium chloride (N) added to 500 c.c. of mud.	Salinity calc. (Parts/100,000).	Salinity obs. (Parts/100,000).	Deviation of salinity obs. from calc. value.
Nil	9·30	9·30	0·00%	7 c.c.	91·13	90·50	—0·69	14 c.c.	172·96	172·00	—0·56
1 c.c.	21·29	21·30	+0·05	8	102·82	102·00	—0·79	15	184·65	184·50	—0·08
2	32·68	32·60	—0·24	9	114·51	114·00	—0·44	16	196·34	197·00	—0·34
3	44·37	44·00	—0·83	10	126·20	124·50	—1·35	17	208·03	206·50	—0·74
4	56·06	57·00	+1·68	11	137·89	136·50	—1·01	18	219·72	219·70	—0·01
5	67·75	66·90	—1·25	12	149·58	147·50	—1·39	19	231·41	230·72	—0·30
6	79·49	79·00	—0·62	13	161·27	160·50	—0·48	Average deviation—0·435%			

TABLE III

Comparision of calculated and experimentally determined salinities.

Mud No.	Salinity calc. (Parts/100,000)	Salinity obs. (Parts/100,000) Arithmetic mean of 100 observations.	Most probable value.	Standard deviation of A. M.	Estimated error of standard deviation.	Mud No.	Salinity calc. (Parts/100,000)	Salinity obs. (Parts/100,000) Arithmetic mean of 100 observation.	Most probable value.	Standard deviation of A. M.	Estimated error of standard deviation.
1	99·02	98·93	98·90	0·551%	0·0551%	4	101·83	101·07	101·10	0·719	0·0719
,,	153·56	152·62	152·60	0·316	0·0316	,,	148·58	148·14	148·10	0·383	0·0383
,,	248·65	247·98	247·95	0·157	0·0157	,,	253·80	252·71	252·80	0·195	0·0195
2	105·82	105·00	105·00	0·539	0·0539	5	101·50	101·87	101·85	0·473	0·0473
,,	152·58	152·12	152·10	0·258	0·0258	,,	155·47	155·36	155·30	0·425	0·0425
,,	246·10	245·73	245·70	0·211	0·0211	,,	235·30	235·33	235·30	0·275	0·0275
3	196·34	196·64	—	0·316	0·070*						

* Mean of 20 observations only.

It is evident from Table III that as the salinity of the mud increases the standard deviation of the arithmetic mean diminishes. With systems having very low salinity the reproducibility would be correspondingly less.

A comparative study of the electrometric and volumetric methods is given in Table IV. The average percentage error of the electrometric method is only +0·37% while that of the volumetric method is −13·35% in one case and −13·60% in the other. In the volumetric methods the filtrate from the mud and not the mud itself, has to be titrated and the lower results obtained by this method seem to be due to the fact that all the chlorine ions present in a mud do not appear in the centrifugate or filtrate obtained under pressure. Results obtained by potentiometric titrations of the filtrates corresponded within the limits of experimental accuracy with those of volumetric measurements.

TABLE IV

Comparison of the electrometric and the volumetric methods of salinity estimation.

(Mud from a typical drilling well—Well A)

Sodium chloride (N) added per 500 c.c. of mud	Salinity calc. (Parts/100,000).	Salinity observed—(Parts/100,000) Electrometric method Salinity.	Electrometric method Deviation.	Volumetric method Pressure filtrate Salinity	Pressure filtrate Deviation.	Centrifugate Salinity.	Centrifugate Deviation.
Nil c. c.	—	7·20	0·00%	6·40	−11·11%	7·05	−2·08%
1	18·89	19·00	+0·58	16·03	−15·14	15·70	−16·89
2	30·58	30·20	−1·24	30·45	−0·42	28·20	−7·78
3	42·27	43·30	+2·44	33·60	−20·51	34·60	−18·15
4	53·96	54·80	+1·56	44·05	−18·37	44·55	−17·44
5	73·25	73·70	+0·61	65·85	−10·10	64·50	−11·95
6	84·94	84·10	−0·99	73·25	−13·76	77·55	−8·70
7	96·63	96·80	+0·18	81·40	−15·24	84·45	−12·60
8	108·32	109·00	+0·63	92·25	−14·84	90·70	−16·27
9	120·01	120·70	+0·57	104·30	−13·09	97·25	−18·96
10	131·70	131·30	−0·30	112·95	−14·24	106·90	−18·83
	Average deviation		+0·367%		−13·35%		−13·60

TABLE V

Mud samples from Well A

Well depth	p_H	Conductivity. (mho).	Ag-AgCl (Electrometric).	Salinity (Parts/100,000) Pressure filtrate.	Centrifugate.
3645 ft.	9·41	$0·835 \times 10^{-3}$	12·5	11·3	11·3
3600	9·30	0·385	11·5	11·1	11·1
3720	9·41	0·788	12·0	11·3	11·3
3750 (Reaming)	9·11	0·794	13·5	12·2	11·4
3750 (Reaming)	9·31	0·820	16·5	12·5	13·4
3767	9·40	0·804	11·5	10·4	9·6
3773-81	9·35	0·788	15·0	12·9	11·3
Not recorded	9·10	0·788	10·5	8·7	7·9
3829	9·15	0·788	10·5	9·2	7·7
3884	9·46	1·056	9·5	9·25	9·2
3884	9·40	1·00	10·5	8·45	9·2
3890 (Reaming)	9·45	0·91	10·0	8·95	9·8
3884-90	9·30	0·851	10·0	8·85	9·35
3900	9·50	0·82	9·5	9·10	9·9
3914 (Reaming)	9·60	0·82	9·5	8·3	8·3
3916	9·60	0·898	9·0	7·35	8·25
3916-24	9·60	0·898	9·5	8·1	8·1
Not recorded	9·55	0·898	10·0	8·85	8·05
3962	9·45	0·791	12·0	12·10	11·3
4005-09	9·35	0·788	10·5	8·80	9·6
Not recorded	9·40	0·788	9·5	8·25	8·05
4039-42	9·45	0·791	8·5	7·20	8·0
4059-69	9·35	0·756	9·0	8·75	9·55
Not recorded	9·40	0·741	8·5	7·20	8·0
4082-92	9·35	0·725	8·5	7·80	7·80
4220-25	9·40	0·741	9·0	8·0	8·0
Not recorded	9·40	0·725	8·0	6·2	7·6
Not recorded	9·35	0·756	7·0	6·3	7·85
4301-16	9·30	0·788	9·5	8·8	8·0
—	9·30	0·772	8·0	8·10	6·45
4321-25	9·30	0·722	7·5	7·20	6·40
4341-46	9·50	0·704	8·0	8·15	8·15
4361-71	9·50	0·526	7·0	6·15	6·45
Not recorded	9·45	0·530	7·0	6·3	6·3
4325-39 (Reaming)	9·35	0·708	8·2	7·05	8·15
Not recorded	9·25	0·824	7·1	6·15	6·80
4326-39 Reaming)	9·40	0·775	6·7	8·20	8·22
4439 (Reaming)	9·45	0·791	7·2	8·20	6·57
4436	9·30	0·935	7·0	6·36	6·37
4439·41	9·20	—	8·0	8·0	7·80
4443	9·35	—	7·5	7·42	7·0
4470	9·40	—	7·5	8·0	7·60
4488-98	9·35	0·859	6·5	6·5	6·5
4510	9·25	0·859	6·3	5·8	5·95
4511-16	9·40	0·825	7·4	6·4	7·35
4560	9·35	0·866	9·4	7·6	8·55

TABLE VII

Mud samples from Well B

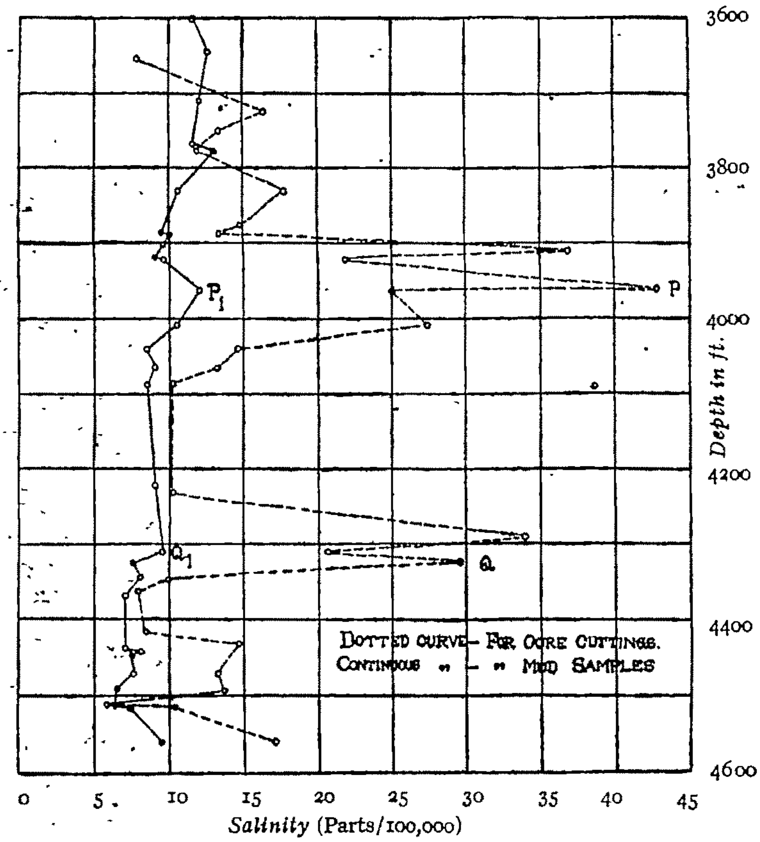
Salinity obs. by Ag-AgCl (Electrometric Method).

Salinity Depth ft.	(Parts / 100,000)	Salinity Depth ft.	(Parts / 100,000)	Salinity Depth ft.	(Parts / 100,000)	Salinity Depth ft.	(Parts / 100,000).
3674	16·5	3820	15·0	4732	12·0	4864	7·0
3678	15·5	3824	15·0	4740-4744	11·0	4868	7·0
3682	15·0	4625	13·0	4744-4748	10·0	4872	6·5
3786	16·0	4629	14·5	4748-4752	9·5	4874	6·0
3790	15·0	4633	14·5	4752-4756	9·5	4883	7·5
3794	15·0	4637	12·5	4764	7·7	4887	7·0
3798	16·0	4643	14·5	4768	7·8	4891	7·0
3802	16·5	4647	13·3	4772	7·5	4895	6·5
3806	15·5	4651	13·2	4776	7·0	4898	6·2
3816	15·0	4655	14·2	4780	8·5		

A series of mud samples was taken at a succession of depths in well A when drilling was in progress and cutting in the mud separated. The mud and cuttings were examined for Cl-content in order to find if there were any significant increases in Cl-concentration which would indicate that a watersand had been penetrated. A similar set of mud samples were taken in well B but the cuttings were not examined. Results of these tests are given in Tables V and VI and Fig. 3. The cuttings curve shows the better defined maxima and minima and a very general correlation exists between the two curves: for example points P and Q in the one curve appear to correspond to points P_1 and Q_1 in the other. Had there been a water-sand in either well with water of relatively high chloride content it seems that it would have shown up in the salinity estimations.

FIG. 3

Salinity records of mud and cuttings (Well A).



C O N C L U S I O N S.

(*i*) The electrometric method gives accurate and reproducible results in salinity determinations in drilling muds.

(*ii*) The volumetric method is unsatisfactory for estimation of chlorides in drilling muds.

(*iii*) When the salinity of water in a watersand is sufficiently high analysis of the mud returns in a well penetrating the sand should indicate accurately the point at which the sand is struck.

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ESTIMATION OF BISMUTH. PART II. TURBIDIMETRIC ESTIMATION WITH BROMATE-BROMIDE MIXTURE

By Anil Kumar Majumdar

Small quantities of Bi (10^{-4} 10^{-6}) have been estimated with bromide-brrmate mixture in a Zeiss turbidimeter with the filters 533.

Bismuth was estimated and separated from lead, copper, zinc, cadmium, etc., by hydrolysis with bromate-bromide mixture by Moser and Maxymowicz (*Z. anal. Chem.*, 1925, **67**, 248). They observed that very small quantities of bismuth can be detected turbidimetrically by the above mixture. This method is more sensitive than the one using sodium sulphide with gum acacia or polyvinyl alcohol as the peptiser (Kurthy and Müller, *Biochem. Z.*, 1924, **149**, 225; Yamamoto, *Bull. Inst. Phys. Chem. Research, Japan*, 1937, **16**, 1312). A marked opalescence was obtained even in so dilute solutions in which the sulphide produced practically no colouration.

The author of the present paper has observed that very small quantities of bismuth even up to the order of 10^{-6} g. can be estimated turbidimetrically.

The turbidity produced when a bromate-bromide mixture was added to a bismuth solution, was measured in a Zeiss Turbidimeter with the filter S 53. Since no selective colour was measured, the wave-length of the filter was not of any particular importance. Wave-length to which the eye was sensitive, was selected.

EXPERIMENTAL

In these experiments only the reagent quality chemicals were used.

Bismuth subnitrate was dissolved in water containing a few c.c. of nitric acid. From a measured volume of this solution the bismuth content was determined by the oxide method (Miller and Van Dyke Cruser, *J. Amer. Chem. Soc.*, 1905, **27**, 116). Solutions, containing different quantities of bismuth per c.c., were prepared by dilutions of a definite volume of this solution. The nitric acid content of these solutions should be kept low either by evaporation of the solution or by neutralisation with sodium carbonate, to avoid generation of bromine the colour of which will affect the analytical results.

Procedure.—A measured volume of the bismuth solution, so prepared, was diluted with water to 20 c.c. in a Jena bottle. To the solution was added quickly 10 c.c. of a bromate-bromide mixture (2·5 g. of KBr and 2·5 g. of $KBrO_3$ in 100 c.c.). The total volume was maintained at 30 c.c. After the addition of the reagent the bottle was shaken for a minute and then allowed to stand for 30-45 minutes when the quantity of bismuth was of the order of $10^{-4}-10^{-5}$ g. and for 3 hours and a half when the quantity of bismuth was of the order of 10^{-6} g. The solution was then taken in the bottle of the turbidimeter and the turbidity, with the filter S 53, was measured against one of the discs, by rotating the right drum, keeping the left drum always at 100. The readings thus obtained with different solutions were plotted against their respective concentrations (Figs. 1—4). From these standard curves the amount of bismuth in an unknown sample was determined. During the measurement with the unknown solution the same disc and the same filter were used.

FIG. 1

Measured after $\frac{1}{2}$—$\frac{3}{4}$ hr. against disc 4

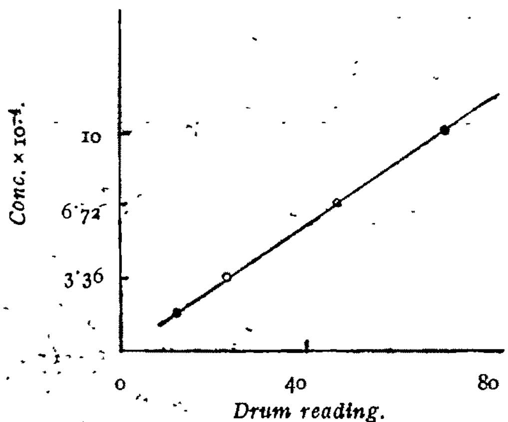


FIG. 2

Measured after 1—$\frac{3}{4}$ hr. against disc 4

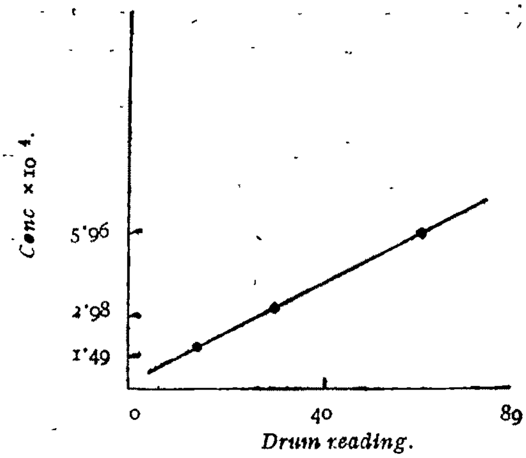


FIG. 3

Measured after $\frac{1}{2}$—$\frac{3}{4}$ hr. against disc 3

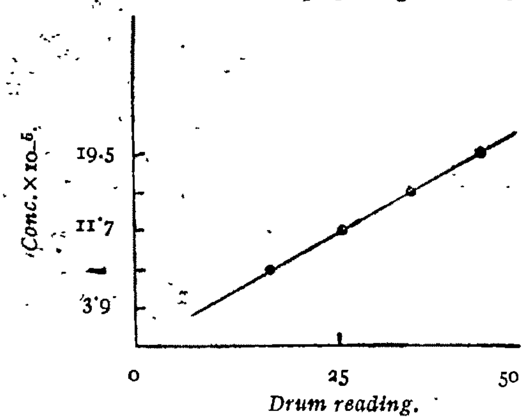
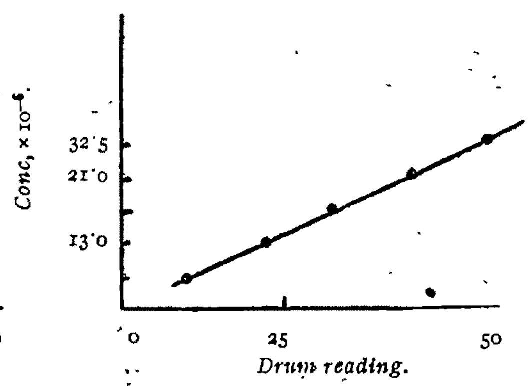


FIG. 4

Measured after $3\frac{1}{2}$ hrs. against disc 1



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MAGNETO-CHEMICAL STUDIES IN VALENCY AND MOLECULAR CONSTITUTION. PART I. *ISO*POLYMOLYBDATES

By Suresh Chandra Das and Priyadaranjan Rây

The formation and the composition of *iso*polymolybdates have been studied by measuring the magnetic susceptibilities of solutions of normal sodium molybdate in aqueous nitric acid of progressively increasing concentration. The susceptibility—p_H curve shows strong deviation from the mixture law and is characterised by having four well-defined inflexion points or breaks, corresponding to the addition of about 4, 7, 9 and 10.5 H-ions for every $6MoO_4$-ions. Formation of *di-*, *para-*, *meta-* and *octo*-molybdates with compositions, as advocated by Jander and co-workers, is thereby confirmed.

The composition and the constitution of the *iso*poly-acids had been a vexed and complex problem in inorganic chemistry for a long time. Copeaux and Rosenheim extended Miolati's scheme of formulation of the heteropoly-acids, based on Werner's theory, to the case of *iso*poly-acids (*cf.* Rosenheim, Abegg's Handbuch, Vol IV, Part I, *ii*, pp. 977-1065, 1921). Subsequent investigations by means of various physical methods have led to a more or less complete elucidation of the problem and placed our knowledge of the subject on a much surer footing. The work of Jander and his co-workers has mainly contributed to this end. The methods deal with the study of the aggregation and degradation processes involved in the formation of these poly-acids. The case of *iso*polymolybdates, with which the present work is concerned, was studied by these workers from a measurement of the rate of diffusion of the polyacid anions formed in solutions of normal sodium molybdate, acidified with nitric acid to progressively increasing H-ion concentrations and containing a large excess of an inert electrolyte ($NaNO_3$). The ionic weights were determined from the observed diffusion coefficients. The results were confirmed by conductometric titration of a solution of normal sodium molybdate with nitric acid. A study of the absorption spectra of progressively acidified solutions of normal molybdate and the thermometric titration of an alkaline or acidified molybdate solution with acid or alkali, as the case may be, furnished additional support to the results derived from the diffusion method (*cf.* Jander, Jahr and Heukeschoven, *Z. anorg. Chem.*, 1930, **194**, 383). The conclusions arrived at by Jander may be summarised as follows:

Normal molybdate	$[MoO_4]^{2-}$	...	Stable between	p_H 14—6·5
Dimolybdate	$[Mo_2O_{11}]^{4-}$	...	,, ,,	p_H 6·3—4·5
Paramolybdate	$[HMo_6O_{21}]^{5-}$	...	,, ,,	p_H 4·5—2·9
Trimolybdate	$[H_2Mo_6O_{21}]^{4-}$	...	,, ,,	p_H 2·9—1·5
Metamolybdate	$[H_3Mo_6O_{21}]^{3-}$	...	,, ,,	
Octomolybdate	$[H_7Mo_{12}O_{41}]^{3-}$	...	,, at about	p_H 1·25

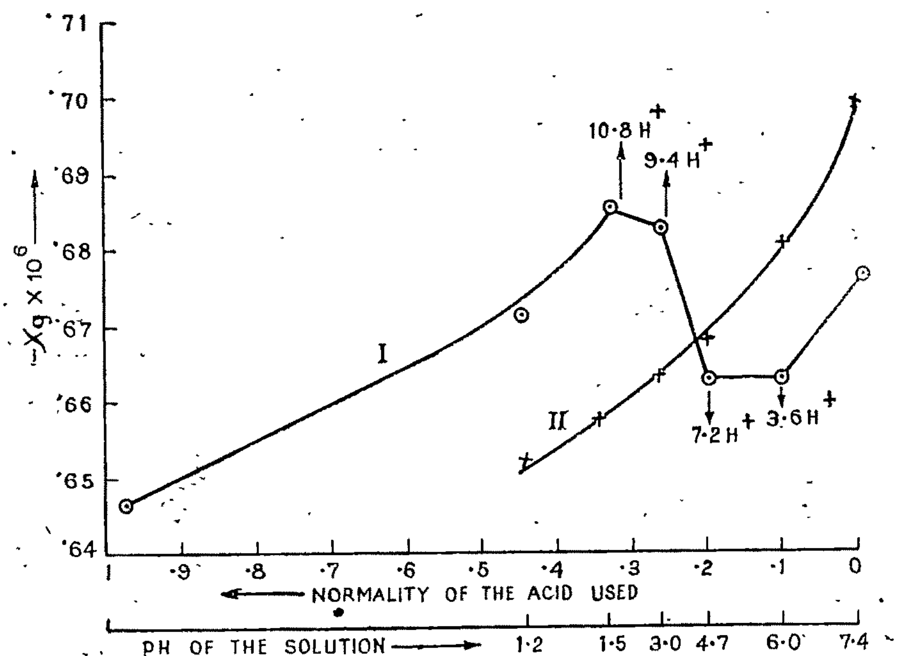
The conductometric titration curve similarly reveals discontinuities corresponding to the addition of 4, 7, 9 and 10.5 H-ions for each 6 MoO_4-ions, originally present in the solution. This indicates the formation of di-, para-, meta- and octomolybdates respectively.

From potentiometric titration of a solution of molybdic acid with KOH, Travers and Malaparade (*Bull. soc. chim.*, 1926, **39**, 1406) obtained evidence for the formation of normal and metamolybdates only.

Britton and German (*J. Chem. Soc.*, 1930, 2154) also carried out potentiometric and conductometric titrations of a solution of normal sodium molybdate with hydrochloric and

other acids, and obtained inflexions on the titration curves corresponding to para-, tri-, meta- and a higher molybdate.

FIG. 1



From conductometric titrations of molybdic acid and sodium molybdate Bye (*Bull. soc. chim.*, 1939, **6**, 174), however, could detect the formation of only normal and metamolybdates in solution.

Brintzinger and Ratanart (*Z. anorg. Chem.*, 1935, **224**, 97), on the other hand, from a measurement of the rate of electrodialysis of ions in acidified molybdate solutions confirmed Jander's results except in the case of his trimolybdate ion, $(Mo_3O_{11})^{4-}$, from a solution of which the dimolybdate crystallises.

In view of this disagreement among different workers about the existence of various polymolybdate ions, it was considered desireable to study the process of aggregation by a new physical method. We have therefore determined the variation of magnetic susceptibility of a solution of normal sodium molybdate, progressively acidified with nitric acid. Every break in the susceptibility—p_H curve indicates deviation from the mixture law and hence points to the formation of a new aggregate in solution, whose composition can be deduced from the difference in the p_H values of the original acid solution and that of the mixture.

EXPERIMENTAL

Pure recrystallised normal sodium molybdate, $Na_2MoO_4 . 2H_2O$, and solutions of chemically pure nitric acid of varying strength from about 1N to 0·1-N were used in these experiments. Sodium molybdate (1g.) was added to every 25 c.c. of the acid solution of any given strength and the mixtures containing the dissolved salt were weighed (Table I). Magnetic susceptibilities of both the individual acid solutions as well as of the mixtures with dissolved sodium molybdate were determined by Guoy's method. The description of the magnetic balance

has been given in a previous paper (Rây and Ghose, *J. Indian Chem. Soc.*, 1943, **20**, 323). Susceptibility of the normal sodium molybdate was also determined in order to calculate the values for the mixture law.

Mass susceptibility (χ_g) corrected for air in each case was calculated from the following formula,

$$\chi_g = \frac{2l \times m'}{m \times H^2 \times 1\cdot019} + \chi_v^{\tau} \,/ d_s$$

The symbols represent values as stated in previous papers. d_s was obtained from the ratio of the weights of water and the solution concerned, occupying the same volume in the measurement tube.

$$l = 11\cdot4 \text{ cm.}, \; H = 10\cdot4 \times 10^3 \text{ gauss.}$$

Table I gives the weights of the mixtures containing 1g. of dissolved $Na_2MoO_4.2H_2O$ in acid solutions of different strength, as well as in pure water.

TABLE I.

Normality of HNO_3-solution ...	0·97	0·44	0·33	0·26	0·20	0·18	0·10
Wt. of the salt + acid solution in g ...	26·61	25·13	25·09	25·09	25·05	25·05	25·05

Wt. of the salt + water in g. = 25·05.

TABLE II

Strength, wt. & D_4^{28} of acid sol.	Pull (-mg.)	$\chi_g \times 10^6$ (neg)	Wt. & D_4^{28} (salt + acid sol.)	Pull (-mg.)	P_H of the mixture	$\chi_g \times 10^6$ (mixture) neg.	H-ions added per $6MoO_4$," from col. 1 & 6	$\chi_g \times 10^6$ mixture law (neg.)
0·97 N	—	—	4·3019 g. (D=1·07)	14·0	<< 1	0·647	—	—
0·44 N 4·1150 g. D=1·027	13·9	0·671	4·2130 g. D=1·057	14·2	1·2	0·671	—	0·652
0·33 N	—	0·677	4·2150 g. D=1·055	14·5	1·5	0·686	10·83	0·658
0·26 N	—	0·683	4·200 g. D=1·054	14·4	3·0	0·683	9·4	0·663
0·20 N	—	0·687	4·204 g. D=1·053	14·0	4·7	0·663	7·26	0·667
0·18 N 4·099 g D=1.023	14·2	0·688	—	—	—	—	—	—
0·10 N 3·6868 g. D=1·002	13·0	0·702	4·203 g. D=1·051	14·0	6·0	0·663	3·63	0·681
Salt solution in water			4·1749 g. D=1·047	14·2	7·4	0·677	—	0·699

The standard value of $-0\cdot72 \times 10^{-6}$ was taken for the mass susceptibility of water. The susceptibility data recorded in the above table represent reproducible values of two independent series of measurements

The results of measurements are summarised in Table II.

The mass susceptiblity for $Na_2MoO_4.2H_2O$ was measured and corrected for air $\chi_g = 0\cdot189 \times 10^{-6}$. From this and that of the acid solution in each case χ_g values for the mixtures employed were calculated on the basis of mixture law according to the formula :—

χ_g (mix.) $= x\ \chi_g$ (salt) $+ (1-x)\ \chi_g$(acid) ; where x = wt. in gram of $Na_2MoO_4.2H_2O$ in one gram weight of the mixture. The values are given in the appropriate column of Table II.

χ_g values for some of the acid solutions were directly measured, while those for others were calculated by interpolation. p_H values for the mixtures were measured in all cases excepting for 0·97*N* by means of glass electrodes. The value for the last named was determined by the indicator method.

DISCUSSION

Since the progressive aggregation of MoO_4-ion occurs through the addition of H-ions, which leads to the formation of various *iso*polymolybdates, the number of H-ions thus removed by interaction with MoO_4'' gives an idea of the composition of the aggregates formed. In Table II are shown the number of H-ions thus removed in different cases for every 6 MoO_4-ions. On plotting the mass susceptibility values for various mixtures against the corresponding p_H values and also against the normality of the original acid solutions employed for making the mixtures, the curve I, as shown in the Fig 1, is obtained. It shows distinct breaks or inflexions at points corresponding to certain p_H values of the mixtures. These points of discontinuity in the susceptibility p_H curve at p_H values of 6, 4·7, 3 and 1·5 are found on calculation to correspond to the interaction with 3·6, 7·3, 9·4 and 10·8 H-ions respectively for every 6 MoO_4-ions of the normal molybdate used. This is in good agreement with the results of conductivity titration and confirms Jander's results of diffusion experiments regarding the composition of *iso*polymolybdates in solution. This is evident from the following representation of the aggregation process that occurs at these transition points.

(i) $6MoO_4'' + 4H^+ \rightleftharpoons 2\,[Mo_3O_{11}]^{4-} + 2H_2O$

(ii) $6MoO_4'' + 4H^+ \rightleftharpoons [HMo_6O_{21}]^{5-} + 3H_2O$

(iii) $6MoO_4'' + 9H^+ \rightleftharpoons [H_3Mo_6O_{21}]^{3-} + 3H_2O$

(iv) $12MoO_4'' + 21H^+ \rightleftharpoons [H_7Mo_{12}O_{41}]^{3-} + 7H_2O$

These represent respectively the di-, para-, meta- and *octo*molybdates of the older classification. No indication of the formation of the trimolybdate could be detected between the para- and meta-molybdates.

The curve II in the figure, which is more or less straight, shows the susceptibility values calculated on the basis of mixture law.

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COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART VIII. COPPER AND NICKEL α-NAPHTHYLBIGUANIDINES

By Priyadaranjan Rây and Harendralal Ray

Copper and nickel α-naphthylbiguanide bases, both hydrated and anhydrous, have been prepared. The complex nickel base has been isolated in three forms, α, β and γ, differing in colour, solubility, melting point and other properties as well as in their state of hydration. Of these, α- and β-forms represent respectively the *cis*- and *trans*-isomers of the planar square nickel complex and γ, their solid solution or molecular compound. Copper α-naphthylbiguanide hydrochloride has also been isolated in two forms.

A series of complex copper naphthylbiguanide salts, *viz.*, chloride, bromide, iodide, sulphate, thiosulphate, dithionate, sulphocyanide, nitrate and carbonate have been prepared and their properties studied. In the case of nickel the only salts prepared and studied were chloride and sulphate

In a previous paper of this series (Rây and Chakravarty, *J. Indian Chem. Soc.*, 1941, **18**, 609) copper and nickel phenylbiguanidines were described. It was found that a number of copper phenylbiguanide salts could be obtained in two modifications, named α and β by the authors, differing in colour, solubility and melting point. The α-varieties were unstable and changed gradually into the β-form. This transformation was accelerated by rise of temperature and the presence of moisture. The β-variety, on the other hand, never changed back into the α-form. From a consideration of their properties the authors concluded that they represent the *cis-trans* isomers of the planar copper complex.

The same authors also succeeded in isolating three varieties of the nickel phenylbiguanide base, α, β and γ, distinguished by their difference in colour, solubility, melting point and other properties. Of these the α-form readily changed into the β-modification. The α- and β-forms were regarded by the authors as representing respectively the *cis*- and *trans*-isomers of the diamagnetic planar nickel complex, whereas the γ-variety was believed to be a solid solution or a molecular compound of the two.

In view of these findings in the case of co-ordination with an unsymmetrical molecule like phenylbiguanide, it was expected that similar isomeric copper and nickel complexes would be more readily obtained with naphthylbiguanide whose structure is more unsymmetrical than that of the phenyl derivative. With this end in view the preparation and the study of the complexes of bivalent metals with α-naphthylbiguanide were undertaken, and this forms the subject matter of the present paper.

Salts of complex copper naphthylbiguanide have not, however, been obtained in more than one modification except in the case of its chloride, which gives two varieties differing in colour. In the anhydrous state one form is chocolate-red (light red-violet when hydrated) and the other violet-blue. They, however, both dissolve in water giving light red solution. Evidences in the present case are therefore not strong enough to consider them as *cis-trans* isomers. They might as well be dimorphs or dimers.

In the case of the nickel complex, however, the nickel naphthylbiguanide base has been isolated in three different forms, α, β and γ, which differ in their state of hydration, colour when dissolved in pyridine, solubility and melting point. The α-form is a flesh-coloured substance and contains one molecule of water which it loses at 110° without any change in its colour. It is

insoluble in water, gives a red solution in pyridine and is sparingly soluble in alcohol. The β-variety forms bright yellow crystals and contains 2·5 molecules of water which it loses at 140° without changing its colour. It is insoluble in water and alcohol, but dissolves in pyridine giving a yellow solution. The γ-form is light buff in colour, contains 2 molecules of water and melts in boiling water. It gives a yellow solution in pyridine.

These observations seem to suggest that, as in the case of the corresponding nickel phenylbiguanide base, nickel α-naphthylbiguanide base can also occur in three forms : α, β and γ. Of these α and β may be regarded to represent respectively the *cis-* and *trans-*isomers of the planar square nickel complex of the penetration type and γ, their solid solution or molecular compound.

The constitution of these copper and nickel naphthylbiguanide complexes can be represented in the same way as those of the corresponding phenylbiguanide compounds.

EXPERIMENTAL

α-Naphthylbiguanide was prepared by heating for about 4 hours aqueous solutions of α-naphthylamine hydrochloride and dicyandiamide in equimolecular proportions and then treating the mixture with an excess of caustic soda solution in the cold. The white crystals of α-naphthylbiguanide separated from the solution. These were purified by recrystallisation from hot water (Cohn, *J. prakt. Chem.*, 1911, *ii*, **84**, 394), m.p., 153·5°—155·5°.

Copper Compounds

Copper α-Naphthylbiguanide Monohydrate.—An ammoniacal solution of copper sulphate in slight excess was added to that of naphthylbiguanide in dilute ammonia and the mixture was well shaken. The light blue-violet crystals, which separated out, were filtered after sometime and washed with water till free from sulphate. This was then dissolved in the minimum quantity of dilute hydrochloric acid and treated with an excess of caustic soda solution in the cold. Thus purified the base was washed with water till free from chloride and dried over lime to a constant weight. [Found: N, 26·16 ; Cu, 11·99. [Cu(Nap Big)$_2$], H_2O requires N, 26·23 ; Cu, 11·92 per cent ; where NapBigH = $C_{12}H_{13}N_5$, a molecule of α-naphthylbiguanide].

The substance forms light blue-violet crystals insoluble in cold water. On boiling with water it melts and slowly dissolves. It is insoluble in cold or hot alkali but is decomposed by mineral acids. In organic solvents like acetone, pyridine, alcohol and ether it dissolves to a pink solution. It behaves as a fairly strong base and liberates ammonia from ammonium chloride. When heated at 90° for about 10 hours it lost whole of its water (3·41% ; calc. 3·37%). The anhydro-base gave on analysis Cu, 12·35. [Cu($C_{12}H_{12}N_5$)$_2$] requires Cu, 12·34%. The anhydro-base has the same colour and other properties as the hydrated variety.

Copper α-Naphthylbiguanidinium Chloride.—An excess of copper chloride solution was added to that of naphthylbiguanide in water. Solid ammonium chloride was then added to the mixture to salt out the complex chloride. The light red-violet crystals separated from the solution. These were washed several times with cold water and dried to a constant weight in air. It is soluble in hot water as well as in pyridine and alcohol, giving a light red solution. {Found: N, 22·70 ; Cu, 10·35 ; Cl, 11·57 ; H_2O (by loss at 115°), 4·41. [Cu(NapBigH$^+$)$_2$] Cl_2, 1·5H_2O requires N, 22·74 ; Cu, 10·33 ; Cl, 11·53 ; H_2O, 4·39 per cent}.

The colour of the anhydrous chloride is chocolate-red. When a solution of the above compound in absolute alcohol was left exposed to air for sometime, blue-violet crystals of the same composition gradually separated from it. These, however, dissolve in water giving a light red solution as the previous compound. {Found: N, 23·93 ; Cl, 12·16 ; Cu, 10·89. $[Cu(NapBigH^+)_2]Cl_2$ requires N, 23·79 ; Cl, 12·06 ; Cu 10·81 per cent}.

The bromide.—An excess of copper chloride solution was added to that of α-naphthyl-biguanide in water. A strong solution of potassium bromide was then added to the mixture. Pale red crystals of the complex bromide separated at once. These were washed and dried as before. The substance dissolves in alcohol and hot water giving a red solution. {Found: Br, 22·96 ; Cu, 9·08. $[Cu(Nap BigH^+)_2]Br_2, H_2O$ requires Br, 23·0 ; Cu, 9·14 per cent}.

The iodide was prepared by adding an excess of concentrated potassium iodide solution to that of freshly prepared complex chloride in the cold. The mixture was thoroughly stirred and allowed to rest. The sparingly soluble chocolate-brown crystals were washed with cold water, dried first over a porous plate and then to a constant weight in air. The substance dissolves in pyridine to a red solution. { Found: I, 32·91 ; Cu, 8·21. $[Cu(NapBigH^+)_2]I_2$ requires I, 32·92; Cu, 8·24 per cent}.

The nitrate.—A strong solution of ammonium nitrate was added to a mixture of naphthylbiguanide and excess of copper chloride in water. The complex nitrate was obtained in the form of sparingly soluble rose-red crystals. These were washed and dried as usual. It dissolves in pyridine giving a violet solution and also in many other organic solvents like alcohol acetone, ether, toluene, etc. {Found : Cu, 9·85 ; NO_3, 19·20. $[Cu(NapBigH^+)_2](NO_3)_2$ requires Cu, 9·91 ; NO_3, 19·32 per cent}.

The Sulphate.—A solution of copper chloride in excess was mixed with that of naphthylbiguanide. From the resulting red coloured solution sparingly soluble light violet crystals of the sulphate were precipitated by adding a concentrated solution of ammonium sulphate. It is soluble in many organic solvents giving a light violet solution. {Found: Cu, 8·60; SO_4, 12·99. $[Cu(NapBigH^+)_2]SO_4, 7H_2O$ requires Cu, 8·60 ; SO_4, 12·98 per cent}.

The thiosulphate.—Pale violet crystals of the thiosulphate were obtained by adding a concentrated solution of sodium thiosulphate to that of the freshly prepared complex chloride. The substance is almost insoluble in water, but dissolves slightly in many organic solvents. {Found: Cu, 9.55 ; S_2O_3, 33·60. $[Cu(NapBigH^+)_2]S_2O_3, 2H_2O$ requires Cu, 9·55 ; S_2O_3, 33·64 per cent}.

The dithionate was prepared by adding a concentrated solution of sodium dithionate to that of a freshly prepared complex chloride. The substance forms pale violet crystals, slightly soluble in hot water and alcohol. {Found: Cu, 8·94; S_2O_6, 44·80. $[Cu(NapBigH^+)_2]S_2O_6, 2H_2O$ requires Cu, 8·91; S_2O_6, 44·85 per cent}.

The sulphocyanide was prepared from a concentrated solution of ammonium sulphocyanide and that of the freshly prepared complex chloride. The pink crystals of the precipitated sulphocyanide were filtered and washed, and then dissolved in absolute alcohol. The solution was filtered and allowed to evaporate in air when pure crystals of the substance were obtained. These were dried in air. {Found: Cu, 10·09; SCN, 18·10. $[Cu(NapBigH^+)_2](SCN)_2$ requires Cu, 10·04; SCN, 18·10 per cent}.

The carbonate was prepared from a concentrated solution of sodium carbonate and that of a freshly prepared complex chloride. The precipitated carbonate was filtered and washed several times with water. Dried first over a porous plate and then in air to a constant weight. {Found :

C, 51·80; H, 4·52; Cu, 11·0. [Cu(NapBigH$^+$)$_2$] CO_3 requires C, 51·93; H, 4·50; Cu, 11·01 per cent}.

The substance forms light violet crystals, insoluble in cold water, but dissolves slightly in acetone and alcohol. In pyridine it forms a red solution.

Nickel Compounds

Nickel α-Naphthylbiguanide and its Hydrate. (*a*) *α-Variety.*—An ammoniacal solution of nickel sulphate in slight excess was added to that of naphthylbiguanide in hot dilute ammonia. After some time the precipitate was filtered and washed several times with water till free from sulphate. The product was dried first on a porous plate and then over alkali to a constant weight. {Found: N, 26·61; Ni, 11·13. [Ni($C_{12}H_{12}N_5$)$_2$], H_2O requires N, 26·48; Ni, 11·10 per cent}.

The substance forms flesh-coloured crystals, insoluble in water. It can displace ammonia from boiling ammonium chloride solution. It is sparingly soluble in alcohol, but dissolves in pyridine giving a red solution. When heated at 110° for about 12 hours it lost the whole of its water (3·40%, calc. 3·41%) and formed the anhydro-base without any change of colour. {Found: Ni, 11·50. [Ni($C_{12}H_{12}N_5$)$_2$] requires Ni, 11·49 per cent}.

(*b*) *β-Variety* was obtained as insoluble yellow crystals by adding a large excess of naphthylbiguanide solution drop by drop to that of nickel chloride at the boiling temperature. The crystals were washed several times with hot water and dried as before. The substance dissolves in pyridine and warm alcohol to a yellow solution. {Found: N, 25·0; Ni, 10·59. [Ni($C_{12}H_{12}N_5$)$_2$], 2·5H_2O requires N, 25·20; Ni, 10·56 per cent}.

On heating the substance at 140° for about 12 hours it lost all its water and formed the anhydro-base without any change of colour. {Found: H_2O, 8·0. Calc. H_2O, 8·09 per cent}.

(*c*) *γ-Variety* was obtained by dissolving the hydrated α-form in the minimum quantity of cold hydrochloric acid and then adding an excess of cold caustic soda solution. The light buff coloured crystalline precipitate was filtered, washed with cold water free from chloride and then dried as before. {Found: N, 25·70; Ni, 10·71. [Ni($C_{12}H_{12}N_5$)$_2$],2H_2O requires N, 25·61; Ni, 10·74 per cent}.

The substance melts when boiled with water. It is sparingly soluble in alcohol, but dissolves in pyridine giving a yellow solution.

Nickel α-Naphthylbiguanidinium Sulphate was obtained as a buff coloured crystalline precipitate by adding a solution of nickel sulphate in slight excess to that of α-naphthyl biguanide. The substance is sparingly soluble in pyridine, acetone and alcohol. {Found: Ni, 9·37; SO_4, 15·30. [Ni (NapBigH$^+$)$_2$] SO_4,H_2O requires Ni, 9·36; SO_4, 15·32 per cent}.

Nickel α-Naphthylbiguanidinium Chloride.—A solution of naphthylbiguanide was added to a hot solution of nickel chloride in calculated amount. The mixture was filtered from any precipitated β-base. The filtrate, on cooling, gave light yellow crystals of the complex chloride. The substance dissolves completely in hot water as well as in pyridine, acetone and warm alcohol. {Found: N, 22·58; Ni, 9·50; Cl, 11·48. [Ni (NapBigH$^+$)$_2$] Cl_2, 2H_2O requires N, 22·59; Ni, 9·47; Cl, 11·46 per cent}.

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A NOTE ON SOLUBILITY METHOD OF DETERMINING DISSOCIATION CONSTANT

By W. V. Bhagwat

Dhar (*J. Amer. Chem. Soc.*, 1913, **35**, 800) has deduced the formula

$$K_2 = \frac{K_1.a.(c-b+a)}{(b-a)^2} \quad \dots \quad (1)$$

for the dissociation of weak acids. This has been verified by several workers for monobasic acids, notably by Dhar and Datta (*Z. Elektrochem.*, 1913, **19**, 407), Bhagawat and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 807), Bhagwat and Doosaj (*ibid.*, 1933, **10**, 477) and by Bhagwat (*ibid.*, 1939, **16**, 235). This work was extended to dibasic acids by Datta and Dhar (*J. Chem. Soc.*, 1915, **107**, 824) and they modified the equation. They showed :—

$$K_2 = K_1. \frac{a[c-2(b-a)]}{(b-a)^2} \quad \dots \quad (2)$$

In our opinion the formula seems to require modification. Consider the reaction with CO_2 solution, that is with H_2CO_3, then we have

$$CH_3COONa + H_2CO_3 \rightleftharpoons CH_3COOH + NaHCO_3$$

Let c be the initial concentration of CH_3COONa, a be the solubility of CO_2 in water and b be the solubility of CO_2 in CH_3COONa of concentration, c, then the excess $b-a$ goes to form CH_3COOH and $NaHCO_3$. Hence finally the moles of CH_3COOH and $NaHCO_3$ formed are $(b-a)$ and $(b-a)$. Thus finally the

conc. of $CH_3COONa = c-(b-a)$; conc. of $CH_3COO' = c-(b-a)$,
(complete ionisation is assumed)

,,	H_2CO_3	a	does not ionise.
,,	CH_3COOH	$b-a$	,, ,, ,,
,,	$NaHCO_3$	$b-a = HCO_3'$	ionises completely.

Now we know that for dissociation constant of acetic acid K_2 we have

$$K_2 = \frac{CH_3COO' \times H^{\cdot}}{CH_3COOH} \quad \dots \quad (a) \qquad \text{also } K_1 = \frac{H^{\cdot} \times HCO_3'}{H_2CO_3} \quad \dots \quad (b)$$

Eliminating $H^{\cdot}$ and substituting the values we have

$$K_2 = \frac{K_1.\ a.\ (c-b+a)}{(b-a)^2} \quad \dots \quad (3)$$

This equation is the same as (1) and not as (2). Moreover, if we assume the reaction to be

$$2CH_3COONa + H_2CO_3 = 2CH_3COOH + Na_2CO_3$$

The molar conc. of		CH_3COOH formed	$=2(b-a)$	
,,	,,	Na_2CO_3	$=b-a$	$=CO_3''$
,,	,,	CH_3COONa (left)	$=c-2(b-a)$	$=CH_3COO'$
,,	,,	H_2CO_3	$=a$	

then as before

$$K_2 = \frac{H^\bullet \times CH_3COO'}{CH_3COOH} \qquad \ldots \quad (a)$$

But here the conc. of H (ion) cannot be determined as before for we only know

$$\frac{H^\bullet \times HCO'_3}{H_2CO_3} = K_1 \text{ (first dissociation).}$$

and

$$\frac{H^\bullet \times CO''_3}{HCO'_3} = K'_1 \text{ (second dissociation).}$$

But we only know CO''_3 and H_2CO_3, but not HCO_3' concentration. We have from above

$$\frac{H^{\bullet 2} \times CO_3''}{H_2CO_3} = K_1 . K_1'$$

or

$$H^{\bullet 2} = \frac{K_1 . K_1' . a}{(b-a)}$$

Substituting the values in (a)

$$K_2 = \sqrt{K_1 . K_1' . \frac{a}{(b-a)}} \left\{ \frac{c-2(b-a)}{2(b-a)} \right\}$$

or

$$K_2 = \frac{\sqrt{K_1 . K_1'}}{2} \; \frac{\sqrt{a}\{c-2(b-a)\}}{(b-a)\sqrt{(b-a)}} \qquad \ldots \quad (4)$$

Even this deduction is different from (2). The author is forced to conclude therefore that the equation of Datta and Dhar (*loc. cit.*) seems to be incorrect.

It will be clear therefore that if we are finding the dissociation constant of a monobasic acid by taking its sodium or potassium salt with the help of a weak acid say n-basic then if we assume the dissociation of the acid H_nB as

$$H_nB \rightarrow H + H_{n-1}B'$$

so that

$$CH_3COONa + H_nB = CH_3COOH + NaH_{n-1}B$$

then we have K_2 as

$$K_2 = \frac{K_1 . a . (c-b+a)}{(b-a)^2}$$

If the dissociation is complete then $H_nB \rightarrow nH + B'^n$

so that $nCH_3COONa + H_nB = nCH_3COOH + Na_nB$

then

$$K_2 = \sqrt[n]{\frac{K_1 . K_1' . K_1'' \ldots n \text{ factors.}}{n}} \; \sqrt[n]{\frac{a/\{c-n(b-a)\}}{(b-a)\sqrt[n]{(b-a)}}}$$

If the acid whose dissociation constant is required is also m-basic and we take the salt Na_mA for this acid H_mA, then if the reaction is

$$Na_mA + H_nB = Na_{m-1}HA + H_{n-1}NaB$$

then we have

$$A'^{m}=c-b+a \text{ and } HA'^{m-1}=b-a$$

also $K_m=\dfrac{H^{\cdot}.A'^{m}}{HA'^{m-1}}$, the m^{th} dissociation constant of the acid. Hence the formula

$$K_2=\frac{K_1.a.(c-b+a)}{(b-a)^2} \quad \dots \quad (5)$$

gives m^{th} dissociation constant provided K_1 is the first dissociation constant where,

$$K_1=\frac{H^{\cdot}H_{n-1}B'}{H_nB} \quad \text{of the acid } H_nB.$$

If the reaction is as $nNa_mA+mH_nB \rightleftharpoons mNa_nB+nH_mA$

Then we have concentration of $H_nB=a$ and that of $B'^{n}=(b-a)$

$$H_mA=\frac{n}{m}(b-a)$$

$$A'^{m}=c-\frac{n}{m}(b-a)=\frac{mc-n(b-a)}{m}.$$

We have for an acid

$$\frac{B'^{n}}{H_nB}.H^{\cdot n}=K_1.K_1'.K_2''\dots\text{to } n \text{ factors.}$$

or

$$H^{\cdot}=\sqrt[n]{K_1.K_1'.K_1'' \quad n \text{ factors}} \quad \sqrt[n]{\frac{a}{(b-a)}}. \quad \dots \quad (x)$$

Similarly

$$\frac{A'^{m}}{H_mA}.H^{\cdot m}=K_2.K_2'.K_2'' \dots . K_m \dots n \text{ factors.}$$

or

$$H^{\cdot}=\sqrt[m]{K_2.K_2'.K_2'' \dots\dots m \text{ factors}} \quad \sqrt[m]{\frac{n(b-a)}{mc-n(b-a)}} \quad \dots \quad (y)$$

Hence for equilibrium, equation (x) = equation (y)

or

$$\sqrt[n]{K_1.K_1'.K_1'' \dots n \text{ factors}} \quad \sqrt[n]{\frac{a}{(b-a)}}$$

$$=\sqrt[m]{K_2.K_2'.K_2''\dots m \text{ factors}} \quad \sqrt[m]{\frac{n(b-a}{mc-n(b-a)}} \quad \dots \quad (6)$$

Clearly this formula does not allow us to calculate the dissociation constants but establishes a relationship among them.

If $m=1$ and $n=1$ then

$$K_1.\frac{a}{(b-a)}=\frac{(b-a)}{c-(b-a)}.K_2$$

or
$$K_2 = \frac{K_1 . a . (c-b+a)}{(b-a)^2}$$

the same formula as given in (1)

If $n=2$ and $m=1$

$$K_2 \frac{2(b-a)}{c-2(b-a)} = \sqrt{K_1 . K_1'} . \sqrt{\frac{a}{(b-a)}}$$

or
$$K_2 = \frac{\sqrt{K_1 . K'}}{2} . \sqrt{\frac{a}{(b-a)}} . \frac{c-2(b-a)}{(b-a)}$$

the same as equation (4).

Doosaj and Bhagwat (*loc. cit.*) have investigated the limits of application of this formula. From theoretical considerations they have established equations which show that the solubility method shows maximum accuracy when the dissociation constants of the acids employed are identical, or are more or less of the same order. These results are supported by their work.

It must be emphasised that in all cases it is assumed that the ionisation of a salt is complete and that of a weak acid is near about zero.

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Erratum

Page	*Line*	*Read*	*For*
93	15 (from bottom)	$CaCl_2$, 0·002*M*	0·001*M*

CRYSTALLINE COMPONENTS OF THE BARK OF *PRUNUS PUDDUM*, ROXB. PART I. IDENTITY OF PUDDUMETIN WITH GENKWANIN

By Duhkhaharan Chakravarti and Ranjit Prasad Ghosh

Three crystalline products have been isolated from the bark of *Prunus puddum*, Roxb. These have m.ps. 278-80°, 150-52° and 237-38° respectively. The compound, m p. 278-80°, which has been named Puddumetin, now appears to be identical with genkwanin (7-methylapigenin), isolated from the Chinese drug, 'Yuen hua'.

Prunus puddum, Roxb. (N. O. Rosaceae) (*Vern.* Phaja, Pajia, Paddam) is a middle-sized or large tree and is often cvltivated in the outer Himalayas from the Sutlej to Sikkim, mostly between 2,500 and 7,000 ft., in the Khasi Hills, Manipur and also in Upper Burma (4,000-6,000 ft.). It flowers early in winter and in spring and the flowers are white, pink or crimson. Its wood is pale red in colour and the bark peels off in horizontal strips. The bark of *P. puddum*, used in this investigation, was supplied by Messrs. G. Ghosh & Co. of Darjeeling.

Three crystalline products have been isolated from the ethereal extact of the bark:

(*i*) A bright yellow light crystalline solid, m.p. 278-80°. It has been named *Puddumetin* (*Science & Culture*, 1942-43, **8**, 463).

(*ii*) A hard shining colourless crystalline substance, m.p. 150-52°.

(*iii*) Shining light yellow needles, m.p. 237-38°. It has been named *Prunusetin*, (Chakravarti and Bhar, *Science & Culture*, 1942-43, **8**, 498).

The constitution of puddumetin is discussed in this paper.

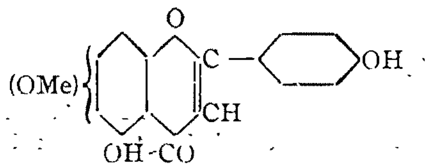
Analytical data of puddumetin are in agreement with the formula $C_{16}H_{12}O_5$. It contains two phenolic OH groups and it forms a colourless diacetyl derivative, m.p. 198-99°. Methoxyl estimation shows the presence of one OMe group, hence puddumetin is $C_{15}H_7O_2(OMe)(OH)_2$.

Puddumetin is insoluble in alkali carbonate and bicarbonate solutions, but dissolves in aqueous solutions of caustic alkalis. On acidification of the alkaline solution the original substance is precipitated. On reducing a cold alcoholic solution of the substance with magnesium and hydrochloric acid a deep orange colour is produced. These reactions indicate that puddumetin is most probably a flavone. The molecular formula of puddumetin agrees with monomethoxy-dihydroxyflavone. Hence it can be represented by the partial formula (I).

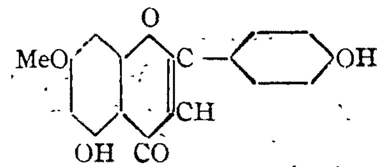
On methylation with methyl iodide puddumetin gives a monomethyl ether, which can be acylated to a monoacetyl derivative, m.p. 194-96°. One of the hydroxyl groups possesses weak phenolic properties and it is found that puddumetin monomethyl ether does not readily dissolve in caustic alkali solution. It is well known that a hydroxyl group in position 5 of the benzopyrone nucleus possesses weak phenolic properties and generally resists methylation. Hence it may be inferred that one of the OH groups of puddumetin is situated at position 5.

Puddumetin is unaffected when a rapid current of air is aspirated through its alkaline solution for more than 2 hours. This excludes the possibility of OH group being present in position 3 of the pyrone ring. The possibility of a methoxyl group being present in 2 position is not, however, definitely excluded. Perkin found that galangin monomethyl ether undergoes aerial oxidation in alkaline solution with formation of benzoic acid and phloroglucinol. Other workers, however, consider that compounds with methoxyl group in position 3 are stable to aerial oxidation in alkaline solution. Thus Bose and Dutta (*J. Indian Chem. Soc.*, 1940, **17**, 46) found that erianthin is stable to aerial oxidation (*cf.* also Bose *et al*, *J. Indian Chem. Soc.*, 1938, **15**, 141; 1939, **16**, 184).

p-Hydroxyacetophenone (m.p. 102-5°) has been obtained by the hydrolysis of puddumetin with alcoholic potash. Consequently puddumetin is a 4′-hydroxylated flavone (II).



(I)



(II)

On demethylation with hydriodic acid puddumetin gives a pale yellow crystalline compound (m.p. 344-46°), which seems to be identical in properties and m p. with apigenin. The m.p. of apigenin is recorded in literature as 343° (Perkin and Everest, "The Natural Organic Colouring Matters"), 347-48° ("Handbuch der Pflanzenanalyse," edited by Klein), Further on acetylation the demethylated product gives a triacetate (m.p. 181-82°) (apigenin triacetate also melts at 181-82°). Hence puddumetin is 7-methylapigenin or genkwanin (II). This conclusion is further supported by the fact that puddumetin monomethyl ether and monoacetyl puddumetin monomethyl ether have the same m.p.s as apigenin dimethyl ether (m.p. 171-72°) and monoacetylapigenin dimethyl ether (m.p. 195-96°) respectively.

The probability that puddumetin is identical with genkwanin was emphasised by Venkataraman (*Science & Culture*, 1942-43, 8, 464), but in absence of an authentic specimen of genkwanin and its appropriate derivatives, and in view of the fact that puddumetin melts at a temperature 6-8° lower than the m p. of genkwanin, it was thought desirable to study the reactions and properties of our compound in greater detail.

Further work on the constitution of prunusetin (m.p. 237-38°) and of the compound (m.p. 150-52°) is in progress.

Experimental

* The powdered bark (600 g.) was extracted with ether in a Soxhlet apparatus for 16 hours. The orange-yellow ethereal solution was concentrated to approximately one-tenth its volume and allowed to stand overnight. A yellow solid separated, which was filtered and the filtrate evaporated until ether was completely removed. A reddish oil which solidified on keeping to a gelatinous mass was obtained.

(*i*) *Isolation of Puddumetin.*—The yellow solid, obtained above, consists of two substances, one being more soluble in alcohol. It was crystallised from a small amount of alcohol, the crystals separating melt at 210-20° and the insoluble residue crystallises again from rectified spirit as yellow needles, m.p. above 270°. The fraction having the lower melting point crystallises from glacial acetic acid as light yellow needles, m p. 225-30° and the fraction having the higher melting point crystallises from glacial acetic acid as deep yellow silky needles, m.p. 278-80° (A).

The oily residue, obtained by evaporating the ethereal filtrate, was dissolved in about four times its volume of hot rectified spirit and the solution was allowed to stand. The solid separating was collected and the filtrate was diluted with water when a fresh crop of solid was obtained. Much difficulty was experienced in filtering this solid due to the presence of slimy

* The constituents have been isolated in collaboration with Mr. Bankim Chandra Bera.

matter. By repeating this procedure the maximum amount of solid was collected and the dilute alcoholic filtrate was rejected. The solids obtained were dried and repeatedly refluxed with benzene when they mostly dissolved, leaving small quantities of yellow or brown residues. The residues were all crystallised from glacial acetic acid, when light brown crystals were obtained, m.p. 225-30°. These together with the light yellow crystals, m p. 225-30°, obtained above, were then extracted several times with boiling acetone and the residue finally left had m.p. above 275° (B). The acetone solution on evaporation gave a solid, m.p. 225-30°. This was extracted thrice with small quantitics of boiling ethyl acetate and the ethyl acetate-insoluble residue (m.p. above 275°) was mixed with residue (B) and crystallised from glacial acetic acid as deep yellow silky needles, m.p. 278-80°, identical with the product (A), total yield 0·04% of the weight of the dry bark.

(*ii*) *Isolation of a compound* m.p. 150-52°.—The benzene solution, obtained above, deposited crystals on standing overnight and further crop of crystals was obtained on concentrating the benzene mother-liquors. These crystals were repeatedly recrystallised from benzene and then from rectified spirit. m.p. 125-30°. On recrystallisation from glacial acetic acid the m.p. rose to 147-50°. Finally it was crystallised from chloroform, when hard lustrous crystals were obtained, m.p. 150-52°. A further crop of crystals, m.p. 150-52°, was obtained from the benzene and chlorofrom mother-liquors by repeating the above process. Total yield, 0·8% of the weight of the dry bark.

From the above mother-liquors on evaporation of the solvents a yellow solid (m.p. 123-24° with contraction at 121°) was left.

(*iii*) The ethyl acetate solution, obtained above, on concentration and cooling deposited crystals, which on repeated crystallisation from ethyl acetate and finally from glacial acetic acid, melt at 237-38°. This has been named *Prunasetin* (Chakravarti and Bhar, *loc. cit.*)

Puddumetin was obtained as deep yellow silky needles, m.p. 278-80°. It is sparingly soluble in ether, benzene and chloroform. It is insoluble in cold alkali carbonate and bicarbonate solutions but is very readily soluble in cold caustic alkali solutions giving yellow colour. An alcoholic solution of the substance gives a brown-violet colouration to ferric chloride solution. It produces an orange colour when reduced in alcoholic solution with magnesium and hydrochloric acid. (Found in a sample dried over P_2O_5 in *vacuum* at 120-30° : C, 67·94 ; H, 4·46 ; OMe, 11·35. $C_{15}H_9O_4$.OMe requires C, 67·6 ; H, 4·23 ; OMe, 10·92 per cent).

Diacetylpuddumetin was obtained from puddumetin with acetic anhydride and pyridine. It crystallises from dilute acetic acid and rectified spirit as colourless silky needles, m.p. 198-99°. (Found in a sample dried over P_2O_5 in *vacuum* at 120-30° ; C, 65·7 : H, 4·53 : OMe, 8·15. $C_{19}H_{13}O_6$.OMe requires C, 65·21 ; H, 4·35 ; OMe, 8·42 per cent). The m.p.s of diacetyl genkwanin have been recorded as 197°98° (Mahal and Venkataraman, *J. Chem. Soc.*, 1936, 569) and 196° (Nakano and Tseng, *J. Chem. Soc. Jap.*, 1932, No. 602, 343, 1933. No. 608, 905).

Puddumetin monomethyl ether was prepared by refluxing for 3 hours a solution of puddumetin (0·1 g.) in dry acetone with methyl iodide (10 c.c.) in the presence of anhydrous potassium carbonate (2 g.). The mixture was filtered and the filtrate evaporated to dryness and the residue crystallised from rectified spirit as light yellow needles, m.p. 171-72°. Its alcoholic solution gives a reddish brown colouration with ferric chloride solution. It does not easily dissolve in caustic alkali solution in the cold, but on boiling dissolves giving a greenish yellow solution. [Found in a sample dried over P_2O_5 in *vacuum* at 100-10° : C, 68·52 ; H, 4·93 ; OMe, 20·36. $C_{15}H_8O_3(OMe)_2$ requires C, 68·45 ; H, 4·69 ; OMe, 20·81 per cent].

Monoacetylpuddumetin Monomethyl Ether (*5-Acetoxy-7 : 4'-dimethoxyflavone*).—It was prepared from puddumetin monomethyl ether using acetic anhydride and pyridine. It crystallised from dilute alcohol as colourless silky needles, m.p. 194-96°. An alcoholic solution of this compound does not give any colouration with ferric chloride solution, nor does it dissolve in cold caustic alkali solution. [Found in a sample dried over P_2O_5 in *vacuum* at 120-30° : C, 67·35 ; H, 4·9 ; OMe, 18·13. $C_{17}H_{10}O_4(OMe)_2$ requires C, 67·06 ; H, 4·70 ; OMe, 18·24 per cent). Monoacetylgenkwanin monomethyl ether melts at 199°.

Attempted aerial oxidation of Puddumetin.—Air was aspirated for 2 hours through a solution of puddumetin in dilute potassium hydroxide solution. The solution was left overnight and on acidification the solid was collected and crystallised from dilute alcohol as yellow needles, m.p. 278-80° (mixed m.p. with puddumetin 278-80°).

Alkaline Hydrolysis of Puddumetin : Isolation of p-*Hydroxyacetophenone.*—A solution of puddumetin (0·2 g.) in alcoholic potassium hydroxide (12·5 g. potassium hydroxide, 25 c.c. water. 30 c.c. rectified spirit) was refluxed for 14 hours on a boiling water-bath. The alcohol was then completely recovered from the solution, the solution was cooled and extracted with ether. The ethereal solution on evaporation left no residue. The alkaline solution was acidified and the solid separating was collected. The yellow acidic filtrate was preserved (A). The solid was treated with sodium bicarbonate solution and the pink insoluble residue was crystallised from dilute alcohol as a brownish solid, m.p. above 270°, which seemed to be unchanged puddumetin. The sodium bicarbonate solution on acidification and extraction with ether gave a very small quantity of a brown solid which could not be crystallised.

The acidic filtrate (A) was extracted with 50 c.c. of ether (in three instalments), the ether evaporated and the pasty brown solid was dissolved in potassium hydroxide solution, carbon dioxide was passed through the solution and the turbid solution extracted with ether. The ethereal extract was dried and ether removed when a small quantity of oil was left which solidified on cooling in ice. It was distilled in *vacuum* and the thick liquid boiling at 95°/0·1 mm. solidified to a crystalline mass, m.p. 99-100°. It crystallised from benzene as colourless shining prisms, m.p. 102-5° (mixed m.p. with an authentic sample of *p*-hydroxyacetophenone) (semicarbazone, m.p. 192-93°, mixed m.p. with the semicarbazone of *p*-hydroxyacetophenone).

Demethylation of Puddumetin with Hydriodic Acid: Isolation of Apigenin.—Puddumetin (0·1 g.) was heated for 3 hours at 130-40° in a glycerine bath with hydriodic acid (sp. gr. 1·7, 10 c.c.) in an atmosphere of carbon dioxide. The mixture was diluted with water and the dark solid separating was collected, washed with sodium thiosulphate solution and water and crystallised from dilute alcohol as light yellow crystals, m.p. 344-46°, yield 0·07 g. Its alcoholic solution gives a dark brown colouration with ferric chloride and when reduced with magnesium and hydrochloric acid in alcoholic solution, it gives a light orange colour.

Triacetylapigenin.—The above demethylated product was acylated with acetic anhydride and pyridine in the usual manner. It crystallises from dilute alcohol as colourless shining silky needles, m.p. 181-82°. (Found : C, 63·80 ; H, 4·49. Calc. for $C_{21}H_{16}O_8$: C, 63·63 ; H, 4·04 per cent).

All analyses recorded in this paper are micro-analyses, carried out by Mr. N. Ghosh, to whom our best thanks are due.

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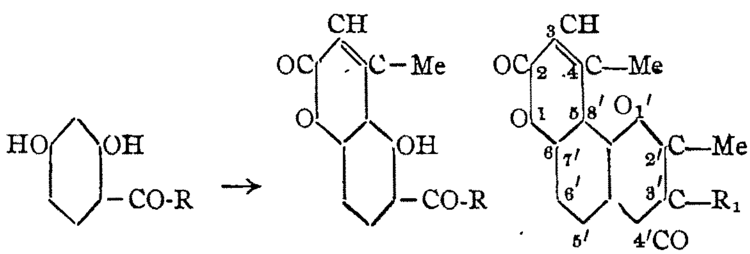
ALUMINIUM CHLORIDE, A NEW REAGENT FOR THE CONDENSATION OF β-KETONIC ESTERS WITH PHENOLS. THE CONDENSATION OF RESACYL AND GALLACYLPHENONES CONTAINING LONG-CHAIN ACYL GROUPS

By M. C. Chudgar and N. M. Shah

4-Acylresorcinols containing long-chain acyl groups have been condensed with ethyl acetoacetate in the presence of anhydrous aluminium chloride, giving the corresponding 5-hydroxy-6-acylcoumarin derivatives in all cases.

In a previous paper (*J. Univ. Bombay*, 1942, **11**, *iii*, 112) the authors showed that 4-stearylresorcinol condensed with ethyl acetoacetate in the presence of aluminium chloride giving 5-hydroxy-6-stearyl-4-methylcoumarin. This reaction has now been extended to other 4-acylresorcinols containing long-chain acyl groups. In this paper the similar condensation of 4-*iso*valeryl-, 4-palmityl-, and 4-lauryl-resorcinols has been described.

All the above ketones condense with ethyl acetoacetate in the presence of aluminium chloride in dry nitrobenzene solution in a manner similar to 4-stearylresorcinol, giving the corresponding 5-hydroxy-6-acyl-4-methylcoumarins (I, $R=C_4H_9$, $C_{15}H_{31}$, $C_{11}H_{23}$ respectively).



(I) (II)

It is interesting to note that all the ketones condense smoothly at 100-110°; if the condensation is effected at higher temperature as done in the previous work (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228, 1066, 1424 *et seq*) there is a considerable diminution in the yield and the product is difficult to purify.

The constitution (I) assiged to the above coumarins follows from the fact that they show exactly similar reactions like 5-hydroxy-6-acylcoumarins described before (*loc. cit.*). They dissolve in alkali with non-fluorescent yellow colour and give colour test with alcoholic ferric chloride, and on Kostanecki acetylation give chromono-α-pyrones (II). It may be mentioned here that 5-hydroxy-6-*iso*valerylcoumarin does not undergo the Kostanecki acetylation. The search of literature does not show any instance of an *iso*-ketone undergoing this reaction.

The above condensation could not be effected with sulphuric acid as condensing agent. 4-Palmityl- and 4-lauryl-pyrogallols do not condense inspite of various attempts

The above results are in harmony with those already obtained previously (*loc. cit.*).

Experimental

Condensation of 4-iso*Valerylresorcinol with Acetocetic Ester in presence of Aluminium Chloride: Formation of 5-Hydroxy-6-*iso*valeryl-4-methylcoumarin* (I, $R=C_4H_9$).—4-*iso*-

Valerylresorcinol, used in this work, was prepared by Nencki's reaction. Resorcinol (3 g., 1 mol.) and ethyl acetoacetate (2·5 g., 1 mol.) were dissolved in dry nitrobenzene (5 c.c.) and added to a solution of anhydrous aluminium chloride (5 g., 2 mols.) in dry nitrobenzene (25 c.c.), the solution being protected from moisture by calcium chloride guard-tube. Copious hydrochloric acid fumes were evolved. The mixture was then heated in an oil-bath at 100-110° for about 1 hour with occasional shaking. When the evolution of acid fumes was negligible, the mixture was cooled, treated with ice and concentrated hydrochloric acid (10 c.c.) and nitrobenzone distilled in steam. A brown oil remained which on treating with little alcohol gave a yellowish powder. This was collected and crystallised from boiling alcohol yielding fine, long, wooly needles, m.p. 127°; yield 1·5 g. (Found: C, 70·0; H, 6·4. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·1 per cent).

The coumarin is sparingly soluble in boiling alcohol and hot acetic acid, and easily soluble in non-hydroxylic solvents. It gives red colour with alcoholic ferric chloride and dissolves in alcoholic alkali with deep yellow colour without fluorescence.

The *acetyl* derivative, prepared by acetic anhydride-pyridine method (refluxing for 6 hours on a water-bath), crystallised from alcohol as needles, m.p. 121°. (Found: C, 68·3; H, 6·4. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0 per cent).

The *oxime* crystallised from acetic acid as small needles, m.p. 223°. The *semicarbazone* separated as needles from alcohol, m.p. 208°.

Clemmensen Reduction of 5-Hydroxy-6-isovaleryl-4-methylcoumarin: Formation of 5-Hydroxy-6-isoamyl-4-methylcoumarin.—The keto-coumarin (1 g.) was dissolved in alcohol and zinc amalgam (20 g.) added. Dilute hydrochloric acid (25 c.c. 1 : 1) was poured in and the mixture heated on a sand-bath. As the reaction proceeded, the coumarin dissolved. After heating for 4 hours a clear solution was obtained; it was filtered off from the unchanged amalgam, which was washed with acetic acid and the washings added to the main filtrate. On cooling, a colourless solid separated. It was collected and crystallised from acetic acid as small needles, m.p. 142°. (Found: C, 73·7; H, 7·8. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3 per cent). The coumarin gives no colour with alcoholic ferric chloride. It is insoluble in aqueous alkali but turns deep yellow and dissolves in alcoholic alkali with deep yellow colour.

Condensation of 4-Palmitylresorcinol: Formation of 5-Hydroxy-6-palmityl-4-methylcoumarin (I, $R=C_{15}H_{31}$).—Dry 4-palmitylresorcinol (2 g.) and the ester (1 g.) were added to aluminium chloride (2 g.) dissolved in dry nitrobenzene (10 c.c.) and the mixture, protected from moisture by $CaCl_2$ guard-tube, was heated as before and then worked up similarly. The solid was crystallised from acetic acid and then from boiling alcohol as silky needles, m.p. 118°, yield 2 g. (Found: C, 75·2; H, 9·4. $C_{26}H_{38}O_4$ requires C, 75·4; H, 9·2 per cent).

The coumarin is sparingly soluble in hot alcohol and acetic acid and easily so in acetone and chloroform. It is insoluble in aqueous alkali but turns deep yellow and gives red colour with alcoholic ferric chloride.

The above condensation could not be effected with sulphuric acid as a condensing agent.

The *acetyl* derivative, prepared as before, crystallised from alcohol as small granules, m.p. 76°. (Found: C, 73·8; H, 8·6. $C_{28}H_{40}O_5$ requires C, 73·7; H, 8·8 per cent). The oxime and semicarbazone could not be prepared owing to the low solubility of the coumarin in alcohol.

Kostanecki Acetylation: Formation of 4 : 2′-Dimethyl-3′-tetradecylchromono-7′ : 8′ : 6 : 5-α-pyrone (II, $R_1=C_{14}H_{29}$).—The coumarin (1 g.), acetic anhydride (10 c.c.) and fused sodium acetate (1 g.) were refluxed on an oil-bath at 150-160° for about 11 hours. The

mixture was then cooled and treated with cold water. The solid obtained was crystallised from boiling alcohol as needles, m.p. 133°. (Found: C, 76·3; H, 8·9. $C_{28}H_{38}O_4$ requires C, 76·7; H, 8·7 per cent). The chromono-α-pyrone is insoluble in alkali and gives no colour with ferric chloride.

Clemmensen Reduction: *Formation of 5-Hydroxy-6-hexadecyl-4-methylcoumarin*.—The coumarin was dissolved in hot alcohol and zinc amalgam (15 g.) added and after the addition of hydrochloric acid was heated on a sand-bath for 4 hours with occasional shaking; the solution was filtered off and on cooling gave a white solid which was collected and crystallised from dilute acetic acid as needles, m.p. 102°. (Found: C, 77·7; H, 10·1. $C_{26}H_{40}O_3$ requires C, 78·0; H, 10·0 per cent). The product turns deep yellow in alkali and gives no colour with ferric chloride.

Condensation of 4-Laurylresorcinol: *Formation of 5-Hydroxy-6-lauryl-4-methylcoumrrin* (I, $R=C_{11}H_{23}$). The resorcinol (6 g.) and the ester (3 g.) were added to aluminium chloride (7 g.) in dry nitrobenzene (30. c.c.) and treated as before. The product, obtained as before, crystallised from acetic acid and then from alcohol as fine needles, m.p. 116-17°, yield 2 g. (Found: C, 73·6; H, 8·5. $C_{22}H_{30}O_4$ requires C, 73·7; H, 8·4 per cent). The coumarin gives yellow colour in alkaline solution and deep red colour with alcoholic ferric chloride.

The *acetyl* derivative, prepared as before, crystallised from alcohol as clusters of needles, m.p. 98°. (Found: C, 71·9; H, 8·1. $C_{24}H_{32}O_5$ requires C, 72·0; H, 8·0 per cent).

Kostanecki Acetylation: *Formation of 4:2'-Dimethyl-3'-decylchromono-7':8':6:5-α-pyrone* (II, $R_1=C_{10}H_{21}$).—The laurylcoumarin (1 g.), acetic anhydride and sodium acetate were refluxed as in the previous case and the product obtained similarly. It crystallised from alcohol, m.p. 154°. (Found: C, 76·1; H, 8·0. $C_{24}H_{30}O_4$ requires C, 75·4; H, 8·0 per cent). It gives no colour with ferric chloride and is insoluble in alkali.

Clemmensen Reduction: *Formation of 5-Hydroxy-6-dodecyl-4-methylcoumarin*.—The coumarin (1 g.) was reduced by zinc amalgam as before. On cooling, the reduction product separated, which was crystallised from dilute acetic acid as needles, m.p. 104°. (Found: C, 76·8; H, 9·2. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·3 per cent). It is insoluble in alkali but turns deep yellow and gives no ferric chloride colour.

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ON THE PREPARATION AND COMPOSITION OF THE ACID CARBONATES OF ALKALINE EARTHS AND LITHIUM

By M. D. Haidar, M. A. Aziz, and P. A. Langer

The acid carbonates of strontium and lithium have been isolated for the first time in the solid state; lithium bicarbonate has been stabilised.

The regularities revealed by periodic classification of elements lead one to expect an order of decreasing stability of the bicarbonates of Cs, Rb, K, Na, Li, Ba, Sr, and Ca. While the bicarbonates of the first four elements are known in the solid state, those of the latter four were believed to exist only in aqueous solution. Attempts were made by Keiser and Leavitt (*J. Amer. Chem. Soc.*, 1908, **30**, 1711) to isolate the acid carbonates of calcium and barium by adding an excess of alcohol and ether to the aqueous solutions of the acid carbonates made by conducting excess CO_2 through a solution of the hydroxides; a white flocculent precipitate was thus formed which rapidly gave off CO_2 and left behind the normal carbonate. They, however, succeeded in isolating the solid compounds at a lower temperature and found them to possess the composition $CaCO_3, 1{\cdot}75H_2CO_3$ and $BaCO_3, 1{\cdot}5H_2CO_3$. They did not extend their researches to other metals. Attempts were therefore made to isolate the acid carbonates of strontium and lithium.

Experimental

Acid Carbonate of Strontium.—The compound was precipitated by mixing ice-cold solutions of strontium chloride and ammonium bicarbonate, the precipitate washed successively with ice-cold water saturated with CO_2, alcohol, and ether, and dried at 0°. On heating to 120° it lost 43·46% of its weight, and the residue was found to contain 70% SrO. $SrCO_3$ contains 70·2% SrO. Hence the composition of the compound can be represented by the formula $SrCO_3, 1{\cdot}60\,H_2CO_3$.

The ratio CO_2 : SrO determined by the method of Keiser and Mac Master (*ibid.*, p. 1715) was found, as mean of three determinations, to be 2·62.

Acid Carbonate of Lithium.—This compound was also precipitated by mixing ice-cold solutions of lithium chloride and ammonium bicarbonate, washed successively with ice-cold water saturated with CO_2, alcohol, and ether, dried, and the ratio $CO_2 : Li_2O$ determined as above, found to be 2·65. The composition of this acid carbonate is thus represented by the formula $Li_2CO_3, 1{\cdot}65\,H_2CO_3$.

An alternative determination of the ratio $CO_2 : Li_2O$ in a solution of acid carbonate of lithium, obtained by passing excess CO_2 through a suspension of Li_2CO_3 in water containing a drop of phenolphthalein solution and agitating the mixture till the pink colour of phenolphthalein just began to reappear, gave the same value as above.

A stable form of lithium bicarbonate was prepared by precipitating a solution of lithium carbonate in carbonated water containing gelatine by means of absolute alcohol. This precipitate did not decompose at the ordinary temperature of the laboratory (25-30°), while the other preparations rapidly decomposed above 0°.

This method of stabilisation is being tried with other unstable compounds.

The CO_2 fixing power of the four elements Li, Ca, Sr, and Ba are given by the formulae $CaCO_3\ 1{\cdot}75H_2CO_3$; $Li_2CO_3, 1{\cdot}65H_2CO_3$; $SrCO_3, 1{\cdot}60H_2CO_3$: $BaCO_3, 1{\cdot}5H_2CO_3$.

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APPLICATION OF HAMMICK AND ANDREWS' EQUATION TO BINARY AND TERNARY MIXTURES

By W. V. Bhagwat and S. Shukla

Hammick and Andrews' equation is extended to ternary mixture of water, urea and acetamide. The values of parachor of acetamide, urea and cane sugar give lower values than the calculated ones.

Hammick and Andrews have shown for binary mixture that the expression

$$P_m = (1-x)\ P + xP$$

gives the parachor P_x of dissolved solid, where P_m, and x have usual significance.

If additive law can be extended for ternary mixture the observed value of parachor for solution P_m is given by

$$P_m = (1-x-y)\ P + xP_x + yP_y$$

where P_x, P_y and P are the parachors of the solutes and solvent respectively and x and y are the molar fraction of the solutes present in $(1-x-y)$ moles of solvent. P_m is given by

$$P_m = \frac{M}{d} r^{\frac{1}{4}}$$

where r is the surface tension of the solution, d, the density of the solution and M is the mean molecular weight of the solution given by

$$M = (1-x-y)M + xM_x + yM_y$$

where M_x and M_y are the moleculer weights of solutes and M is the molecular weight of solvent.

Parachor of acetamide is determined in the fused state by Sudgen (*J. Chem. Soc.*, 1924, **125**, 1177) and by Turner and Merry (*ibid.*, 1910, **97**, 2068). The value is 148·8. The calculated value is 150·8. The average value in solution as obtained by us is 130, much lower. The same is true of urea. The calculated value is 141·2, but the observed value increases with concentration and is about 118. Assuming this value for urea in solution the value for acetamide in ternary mixture is calculated. It comes out to be 134, very near to the value obtained in solution. In the follwing tables parachor of water has been taken to be 52·2.

Table I

Parachor of acetamide

	x=0·1792.		M_m=25·34.		x=0·2280.		M_m=27·35.		x=0·2818.		M_m=29·55.	
Temp.	Density.	r.	P_m.	P_x	Density.	r.	P_m.	P_x.	Density.	r.	P_m.	P_x.
20°	1·049	54·12	65·51	126·4	1·053	52 48	69·92	129 9	1 059	50·74	74·47	131·2
30	1·043	52·06	65·25	125·02	1·047	50·48	69·63	128·6	1·053	48·77	74·15	130·0
40	1·038	50·82	65·18	124·6	1·041	49·00	69·50	128·7	1·047	46 99	73·87	129·1
50	1·033	49·11	64·94	123 0	1·036	46·76	69·00	125·8	1·041	45·36	73·65	128·3

Parachor of urea

	x=0·0453.		M_m=19·81.		x=0·0792.		M_m=21·33.		x=0·0987.		M_m=22·15.	
Temp.	Density.	r.	P_m.	P_x.	Density.	r.	P_m.	P_x.	Density	r.	P_m.	P_x.
20°	1·059	69·66	54·05	93·05	1·083	70 76	57·12	114·3	1·095	70 76	58 69	117·9
30	1·054	68·06	53·96	91·06	1·079	69·1	57·02	113·1	1·090	68·55	58·49	115·9
40	1 051	65 94	53·63	83·8	1 074	67·05	56·83	110·7	1·085	66·49	58·32	114·5
50	1·047	64·06	53·52	81·8	1·071	65·1	56·57	107·4	1·083	65·04	58 12	112·2

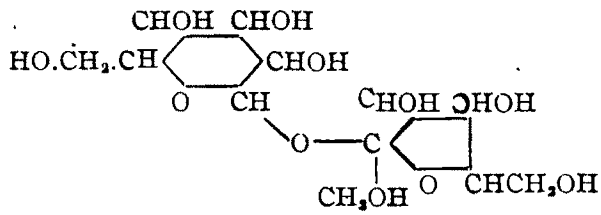
	x=0·1501.		M_m=24·27.		x=0·1245.		M_m=23·23.	
Temp.	Density.	r.	P_m.	P_x.	Density.	r.	P_m.	P_x.
20°	1·132	70·04	62·01	117·6	1 113	70·44	60·47	118 6
30	1 127	68·41	61·93	117·0	1·109	68·32	60 24	116·8
40	1·122	66·36	61·73	115·7	1·106	66·19	59·92	114·2
50	1·117	64·51	61·58	114·7	1·102	64·68	59·8	113·2

TABLE I (*contd.*)

Parachor of cane sugar

	x=0·0216.		M_m =25·02.		x=0·0257.		M_m =26·35.		x=0·0377.		M_m =30·27.	
Temp	Density.	r.	P_m.	P_x.	Density.	r.	P_m.	P_x.	Density.	r.	P_m.	P_x.
20°	1·148	70·46	63·13	558·5	1·167	70·63	65·46	567·8	1·217	71·58	72·35	586·6
30	1·144	68·21	62·84	544·9	1·163	68·80	65·25	560·0	1·213	69·24	71·97	576·6
40	1·141	66 59	62·73	539·8	1·159	67·17	65·11	554·6	1·208	67·72	71·90	574·6
50	1 136	66·31	62·70	538·6	1·156	66·16	65·07	553·8	1·205	65·22	71·66	568·4

The cane sugar is $C_{12}H_{22}O_{11}$. Hence its parachor should be $P=12C+22H+C_{12}H_{22}O_{11}$ $110+\text{Ring of six}+\text{Ring of five}=57·6+375·2+220+6·1+8·5=667·4$



Parachor of a Ternary mixture—Water, Acetamide and Urea

TABLE II

2·725 G. of urea and 5·354 g. of acetamide dissolved in 7·5025 g. of water. x (acetamide) $=0·1640$. y(urea)$=0·0821$. $1-x-y$ (water)$=0·7539$. M_m =28·18.

Temp.	Density.	r,	P_m.	P_x.
20°	1·070	52·08	70·74	132·2
30	1·066	50·07	70·33	130·7
40	1 060	48·44	70·3	131·3
50	1·056	47·18	69·93	130·2

TABLE III

4·4160 G. of urea, 5·3444 g. of acetamide dissolved in 7·4446 g. of water. x(acetamide) $=0·1567$. y(urea)$=0·1274$. $1-x-y$ (water)$=0·7159$. M_m =29·78.

Temp.	Density.	r.	P_m.	P_x.
20°	1·095	52·58	73·24	133·3
30	1·090	50·67	72·91	131·7
40	1·083	49 39	72·274	131·6
50	1·078	47 77	72·64	131 8

TABLE IV

2·7626 G. of urea, 9852 g. of acetamide dissolved in 7·4617 g. of water. x (acetamide) = 0·2627. y(urea)$=0·0737$. $1-x-y$ (water)$=0·6636$. M_m =3187.

Temp.	Density.	r.	P_m.	P_x.
20°	1·071	48·94	78·66	134 4
30	1·069	46·77	77·98	132·4
40	1·053	45 60	77 69	131·7
50	1·056	44·10	77·78	132·7

TABLE V

3·5402 G. of urea and 7·2818 g. of acetamide dissolved in 7·423 g. of water. x (acetamide)$=0·2875$. y(urea)$=0·0992$. $1-x-y$ (water)$=0·6933$. M_m =30·67.

Temp.	Density.	r.	P_m	P_x.
20°	1 078	53 92	76·35	136·5
30	1·072	51·75	76·03	136·1
40	1·068	50·06	75·82	136 5
50	1·063	48·49	75·58	135·7

These results clearly show that the law can be extended to ternary mixtures. Clearly the values assumed are those which were obtained in solution. The coincidence between the results obtained in mixture and when studied alone in solution is enough to prove the applicability.

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ON THE CONSTITUTION OF NATURAL COUMARINS ISOLATED FROM *LUVANGA SCANDENS*, HAM

By Prafulla Kumar Bose and (Miss) Asima Mookerjee

The berries of *Luvanga scandens* Ham. (Family *Rutaceae*) are sold in the bazzars of Bengal under the name of Káklá. They are an important constituent of the "Group of eight remedies" of the Ayurvedic system of medicine, according to which 'the root and berries are sweet, oily and cooling; allay thirst; cure consumption and biliousness; aggravate kapha.' They are further used for preparing a perfumed medicinal oil.

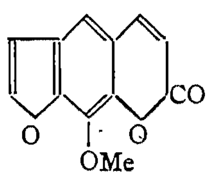
The rinds of the berries contain numerous oily glands, the oil of which is more or less stimulating, tonic and fragrant.

The present paper describes the constituents of the berries which were procured from the local market. These were identified by Prof. A. Das-Gupta of the Bangabasi College, Calcutta, to whom our best thanks are due.

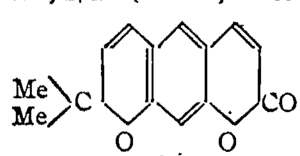
The crushed berries on extraction with petroleum ether gave a greenish brown oil from which four crystalline neutral compounds have been isolated. No alkaloid could be detected in the berries. It should be mentioned in this connection that only the *matured fruits yield the compounds described below but these are totally absent in unripe samples.*

(1) A colourless compound, m.p. 145°, crystallising in long, slender, colourless needles, was obtained in a yield of 0·1–0·4%. It is neutral to litmus, indifferent towards ferric chloride and shows no optical activity. It is insoluble in dilute aqueous alkali, but dissolves in concentrated sulphuric acid with a stable yellow colour. An alcoholic solution of the substance turns yellow on the addition of aqueous alkali, and the alkaline solution remains clear on dilution with water. Acidification precipitates the original substance, thus apparently the substance behaves like a coumarin.

The analytical data are found to agree with the formula $C_{11}H_5O_3(OMe)$. The properties of the compound as also the observed analytical values indicate agreement with those of xanthotoxin (I) which was first isolated from *Fagara xanthoxyloides*, Lam (Thoms, *Chem. Ztg.*, 1910, **34**, 1279) and later on from *Ruta chalepensis*, Linn (Brandt, *Dissertation, Berlin*, 1915).



(I)



(II)

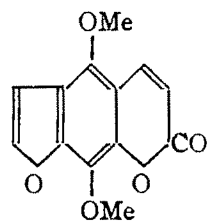
The identity of compound (I) with xanthotoxin could be definitely established by a direct comparison and the mixed m.p. of the two substances, an authentic specimen of xanthotoxin being received from Professor E. Späth of Vienna, to whom our best thanks are due.

(2) The second substance, m.p. 128°, forms stout, rhombic plates and is obtained in a yield of 0·05–0·06%. It gives orange-red colour with cold concentrated sulphuric acid. The compound is neutral and indifferent towards ferric chloride. It is insoluble in aqueous alkali but dissolves in alcoholic potassium hydroxide from which the original substance is precipitated by acidification. Thus it behaves as a coumarin.

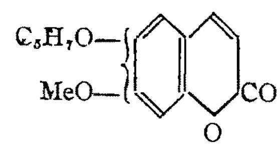
The observed C-H values and molecular weight agree with the formula $C_{14}H_{12}O_3$. It is optically inactive and does not contain any methoxy group. We thought that the compound might be identical with xanthyletin (II) which has been isolated so far only from *Xanthoxylum americanum*, Mill (Robertson and Subramanium, *J. Chem. Soc.*, 1937, 286; Bell and Robertson, *ibid.*, 1936, 1828; Dieterle and Kruta, *Arch. Pharm.*, 1937, **275**, 45).

The tetrahydro derivative of the coumarin has been prepared by catalytic hydrogenation with palladium-charcoal, and the reduction product, thus obtained, is found to have the same m.p. 158·5° as tetrahydroxanthyletin and both of them show no depression in their mixed melting points. The identity of the second compound of *L. scandens*, with xanthyletin has been established under the joint investigation with Späth and Dobrovolny (*Ber.*, 1939, **72**, 1450).

(3) The third neutral substance melts at 151-52° and has the formula $C_{11}H_4O_3(OMe)_2$. This is supposed to be a coumarin derivative from its behaviour and properties. A close inspection of the properties of this compound suggests its identity with *iso*pimpinellin (III) (Hent, *Arch. Pharm.* 1898, **236**, 162: Wessely and Kallab, *Monatsh*, 1932, **59**, 16). A direct comparison has been made between the two substances, *iso*pimpinellin being obtained



(III)



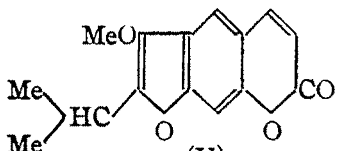
(IV)

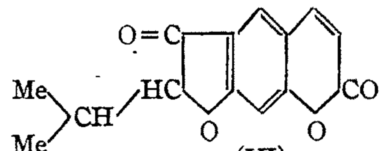
from *Pimpinella saxifraga*. The properties of the two compounds are identical and a mixture of the two also melts at 151-52°.

(4) The fourth compound (yield 0·08–0·5%) is a new substance and has been named "luvangetin." It forms colourless plates, m.p. 108-109°. It could be obtained pure with considerable difficulty (*vide* experimental). The method of purification consists in slow crystallisation of the crude substance and subsequent separation of luvangetin from other constituents by hand-picking.

The C-H values and the molecular weight show that luvangetin has the formula $C_{15}H_{14}O_4$. Methoxy estimation by Zeisel-Pregl Vieböck's method proves the presence of one methoxy group. On the catalytic hydrogenation with palladium-charcoal, luvangetin gives a dihydrocoumarin, m.p. 131°, having the formula $C_{15}H_{16}O_4$. Luvangetin is optically inactive and is found to share many of the properties of coumarin. It is neutral to litmus, but dissolves in alcoholic potassium hydroxide with a yellow colour. The substance is precipitated from the alcoholic solution on acidification, but not on dilution with water. It dissolves in concentrated sulphuric acid with an orange-red colour. The formula of luvangetin therefore can be written as (IV). Since luvangetin does not respond to acetylation or tests for the ketonic group, OH or CO group may be assumed to be absent. The insolubility of luvangetin in dilute aqueous potassium hydroxide and its indifference towards ferric chloride prove the absence of a phenolic OH group in the molecule. In the absence of any direct proof of the function of the fourth oxygen atom, it is assumed to be of the ether type.

The analytical data of luvangetin and its properties suggested at first its identity with peucedanin (Jassoy and Haensel, *Arch. Pharm.*, 1898, **236**, 663) (V).

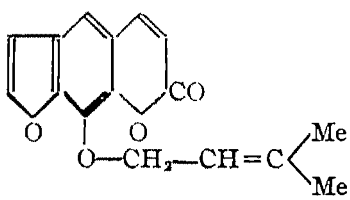

(V)


(VI)

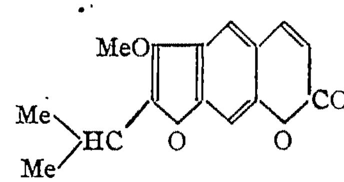
But a close inspection of the properties of luvangetin, however, revealed that it is different from peucedanin. The latter is easily demethylated by means of concentrated hydrochloric acid at room temperature to oreoselon (VI) (Späth, Kläger and Schlösser, *Ber.*, 1931, **64**, 2207) whereas luvangetin remains unchanged under similar experimental conditions.

The C_5H_7O residue might originate from isoprene molecule, Many natural coumarins have been proved to be condensation products of isoprene with substituted coumarins. The isoprene unit might be present in various forms, the possible types of which are represented by the following :

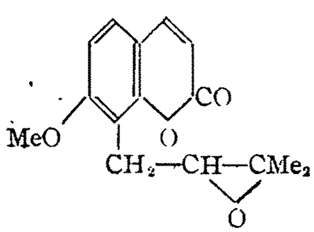
(i)


(Imperatorin)

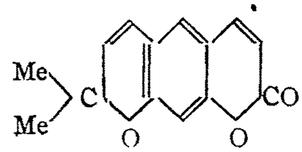
(ii)


(Peucedanin)

(iii)

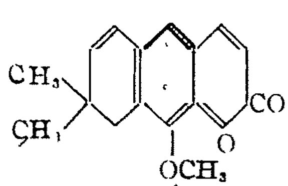

(Aurapten)

(iv)


(Xanthyletin)

Of these the first type is out of consideration in the present case, since coumarins containing phenoxy groups, $Me_2C=CH—CH_2O—$get readily hydrolysed by concentrated sulphuric acid in glacial acetic acid into phenolic compounds (Späth and Klager, *Ber.*, 1933, **66**, 920).

Luvangetin under similar experimental conditions does not give any phenolic substance. Like other furocoumarins (e.g., Imperatorin, *vide supra*) luvangetin does not give rise to furan-2 : 3-dicarboxylic acid on oxidation with alkaline hydrogen peroxide, and therefore it does not contain any unsubstituted furan ring.


(VII)

Glycide ring structure for luvangetin, as shown in type (iii) is quite unlikely as the molecular formula in that case would become $C_{15}H_{16}O_4$ in place of $C_{15}H_{14}O_4$: the observed

C-H values, however, agree better with the latter formula. Moreover, a compound of the type (iii) would be expected to undergo hydrolysis to a dihydroxy compound by means of aqueous oxalic acid (Späth and Klager, *Ber.*, 1933, **66**, 914).

Type (ii) and (iv) might suggest a possible solution of the constitution of luvangetin.

It has been settled in a joint work with Späth and his co-workers (*Ber.*, 1940, **73B**, 1361) that luvangetin has the structure of type (iv) (e g. VII) and this has been definitely confirmed by its synthesis (Späth and Schmid, *Ber.*, 1941, **74B**, 103).

EXPERIMENTAL

Test for Alkaloid.—60 G. of the crushed berries were extracted with rectified spirit in a Soxhlet for 15 hours. The extract was freed from the solvent under reduced pressure and the residue poured into 1% acetic acid solution (200 c.c.). The mixture was extracted with ether and its aqueous portion filtered The clear filtrate was made alkaline with ammonia and extracted with ether. Removal of ether left a trace of oily matter which did not give appreciable precipitate with acidified potassium bismuth iodide solution.

Isolation of the Coumarins.—Matured berries (2·5 kg) of *L. scandens* were crushed in a mortar with purified sand. The mixture was extracted with petroleum ether (b.p. 40-60°) for 24 hours in a Soxhlet. The product was allowed to stand overnight and then filtered to remove a crystalline deposit and tarry matters (Fraction P). The clear filtrate was freed from the solvent on the water-bath and the brown syrupy liquid was allowed to stand in a cool place for about a week. The crystals (Fraction Q) which separated out were collected and washed with petroleum ether and dried on a porous plate. The filtrate was worked up for further quantities of coumarins following essentially the method of Späth and Socias (*Ber.*, 1934, **67**, 59), thus :

The oil was cooled to about 15° and to it was added 200 c.c. of 20% methyl alcoholic potassium hydroxide with constant shaking. The mixture was allowed to stand for 45 minutes, at the same temperature and then poured into 1.5 litres of ice-water. The mixture was then extracted with ether. The aqueous portion was acidified with hydrochloric acid (congo red) and distilled in vacuum to remove the greater portion of methyl alcohol and allowed to stand overnight. The separated oil was extracted with ether and the ethereal solution was twice washed with 100 c.c. of 25% aqueous potassium carbonate solution and then with water. The ether layer was then dried over sodium chloride and the solvent removed. The residue solidified on keeping in an ice-chest for a few days. This was washed with petroleum ether and dried over a porous tile to remove adhering oil (Fraction R).

Purification of Fraction P : Isolation of Xanthotoxin.—This fraction was washed with cold 90% methyl alcohol to remove tarry matters. The crystalline residue was then repeatedly crystallised from alcohol and finally from benzene-petroleum ether, till the m.p. became constant at 145°. For analysis a portion was distilled at 140-45°/0·05 mm. and crystallised from benzene-petroleum ether. (Found : C, 66.43 ; H, 4.00 ; OMe, 14.40. $C_{12}H_8O_4$ requires C, 66·67 ; H, 3·70 ; OMe, 14.35 per cent). The yield amounted to nearly 2.3 g. Mixed with a specimen of pure xanthotoxin, m.p. 145°, there was no depression of melting points.

Isolation of Luvangetin.—The Fraction Q and the Fraction R were mixed together and twice crystallised from hot methyl alcohol when pale yellow crystals (Fraction S) were obtained. The mother liquors gave on slow evaporation transparent plates and soft needles along with a little oily matter. The mixture was collected, washed with a little cold 80% methyl alcohol, and recrystallised from methyl alcohol very slowly. The plates and

needles, which separated out, were collected, washed with a little cold methyl alcohol and then separated from each other mechanically. The plates and needles were then crystallised separately from the same solvent, when 0·2 g. of xanthotoxin (needles), m.p. 144°, were obtained. The plates are those of luvangetin and had m.p. 107-8°.

The Fraction S was repeatedly crystallised from pure methyl alcohol when pale yellow opaque crystals, m.p. 121° (Fraction X) were obtained. The mother-liquors were allowed to evaporate slowly at room temperature in separate vessels, when transparent plates mixed with varying quantities of opaque crystals separated. These were freed from the mother-liquor (Fraction Y) which was kept for further investigation. These were separated from each other by hand picking and the two varieties were crystallised separately in a similar manner. This operation took a considerable time. The transparent four-sided plates were then distilled at 145-55°/0·03 mm. (a small fraction distilling below 140° was rejected). The colourless distillate soon solidified and was recrystallised from acetone-petroleum ether, m.p. 108°. Recrystallisations from alcohol, ether or chloroform-petroleum ether did not raise the m.p. The substance is easily soluble in hot alcohol, chloroform, acetone, acetic acid and hot benzene. From benzene luvangetin separates as colourless plates, m.p. 102-4°. This substance when dried in vacuum over phosphorous pentoxide suffered a loss in weight, became opaque and the m.p. rose to 108°. Apparently luvangetin crystallises from benzene with benzene of crystallisation. (Found in sample dried in vacuum at 80°: C, 69·85, 69·63; H, 5·22, 5·44; 5·47; OMe, 11·76. M.W. by Rast's method in camphor, 242. $C_{15}H_{14}O_4$ requires C, 69·73; H, 5·42; OMe, 12·02 per cent. M.W., 258). The yield of pure luvangetin amounted to 2·0 g.

Isolation of Xanthyletin from the Fraction (X).—The opaque crystals (*vide supra*) were distilled in vacuum at 130-40°/0·03 mm and twice crystallised from acetone-ether, when colourless stout rhombic crystals, m.p. 128° (yield 0·1 g.) were obtained. (Found: C, 73·25; H, 5·47; M.W. by Rast's method in camphor, 232. $C_{14}H_{12}O_3$ requires C, 73·68; H, 5·26; M.W. 228). The substance on catalytic hydrogenation yields a tetrahydro derivative, m.p. 158° which showed no depression in m.p. with tetrahydroxanthyletin, m.p. 158°.

Isolation of Iso*Pimpinellin from the Fraction Y.*—The solids separated from the fraction Y (*vide supra*) were repeatedly crystallised from different solvents when the m.p. could not be raised above 151-152°. Mixed with a specimen of *iso*pimpinellin it showed no depression in m.p.

Action of Acetic Anhydride on Luvangetin.—Luvangetin (0·1 g.) was boiled with 3 c.c. of acetic anhydride and 9·5 g. of freshly fused sodium acetate for 4 hours. The mixture was poured into cold water, neutralised with sodium bicarbonate and extracted with ether. The residue left after the removal of the solvent was crystallised from ether. m.p. 107-8°. No depression was observed on mixing with pure luvangetin.

Action of Oxalic Acid on Luvangetin.—Luvangetin (0·2 g.) and oxalic acid in 7 c.c. of water were boiled under reflux for 2 hours. The mixture was cooled and the crystals extracted with chloroform. The chloroform solution was dried over sodium chloride, concentrated and diluted with petroleum ether, when colourless crystals, m.p. 107-8°, were obtained. Mixed with luvangetin, the m.p. was found to be the same.

Action of Dilute Alkali on Luvangetin.—Luvangetin (0·1 g.) and pure methyl alcohol (5 c.c) was mixed with 40 c.c. aqueous 1% potassium hydroxide and the solution was refluxed on the water-bath for half an hour. The yellow solution gradually became brown. It was

acidified with dilute hydrochloric acid, kept overnight and extracted with ether. The residue from the ethereal solution was distilled in high vacuum (140-45°/0·03 mm.) and crystallised from ether. The plates melted at 108° alone or mixed with a pure specimen of luvangetin.

Attempts to dehydrogenate Luvangetin with Palladium Black.—(*a*) Luvangetin (0·2 g) was heated with palladium black (0·6 g.) for 4 hours at 100°-2° in vacuum (2 mm. pressure). Distillation of the product in vacuum (140-45°/0·03 mm.) gave a liquid distillate, which on crystallisation from acetone-petroleum ether melted at 108° and was identified as luvangetin by the mixed m.p. method. (*b*) A similar experiment was carried out at 180° under ordinary pressure for 8 hours. In this case too unchanged luvangetin was recovered in a yield of over 80%.

Oxidation of Luvangetin by Alkaline Hydrogen Peroxide.—Luvangetin (0·1 g.) was dissolved in aqueous potassium hydroxide (10 c.c. 5%) and 5 c.c. of 8% hydrogen peroxide added. The mixture was left for 15 hours and then heated on the water-bath to decompose the excess of H_2O_2. The solution was cooled, just acidified with hydrochloric acid and made faintly alkaline with ammonia. Addition of a few drops of calcium chloride precipitated calcium oxalate which was filtered off. The clear filtrate was again acidified with hydrochloric acid and thoroughly extracted with ether. The residue from the dry ethereal solution did not crystallise. Distillation in high vacuum did not give any fraction which could be crystallised.

Catalytic Hydrogenation of Luvangetin.—Luvangetin (0·2 g.) dissolved in methyl alcohol, (10 c.c.) was shaken with 0·1 g. of 25% palladium-charcoal catalyst (which had been previously saturated with hydrogen) in an atmosphere of hydrogen. 175 C.c. of hydrogen were absorbed within a few minutes at 22° and 766 mm. ($C_{15}H_{14}O_4$ requires 18·4 c.c. at 22° aud 766 mm.). The solution was freed from the catalyst and the solvent removed. The resulting crystalline mass was distilled at 140-50°/0·04 mm. The distillate (0·2 g.) was crystallised from acetone-petroleum ether when shining plates, m.p. 131°, were obtained. (Found: C, 69·55; H, 6·38, OMe, 11·02. $C_{15}H_{16}O_4$ requires C, 69·23: H, 6·15; OMe, 11·92 per cent). It gave a yellow solution with cold concentrated sulphuric acid.

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Received April 6, 1944.

ESTIMATION OF BISMUTH. PART III. VOLUMETRIC ANALYSIS WITH PHENYLARSONIC ACID

By Anil Kumar Majumdar

In a previous paper (Part I of this series, *J. Indian Chem. Soc.*, 1944, **21**, 119) it was shown that bismuth could be estimated gravimetrically by the reagent phenylarsonic acid and separated from elements such as silver, lead, mercury, copper, cadmium, tin, cobalt, nickel, zirconium, thorium, thallium, alkalis and alkaline earths by precipitattng at a p_H of 5·2 to 5·3 in acetic acid solution, buffered with sodium or ammonium acetate.

The precipitate bismuth phenylarsonate can be used for the volumetric estimation of bismuth by dissolving it in hydrochloric acid, and reducing by hydriodic acid the pentavalent arsenic of phenylarsonate to trivalent state, which is again being oxidised by iodine solution. The method followed here is almost the same as that of Kolthoff (*Z. anal. Chem.*, 1923, **62**, 137) recommended for the estimation of arsenic acid, with a little modification.

Experimental

Bismuth was precipitated by the reagent following the procedures described in Part I of this series and using the same reagents. The precipitate thus obtained was well washed with hot water and transferred to a conical flask with water and concentrated hydrochloric acid in equal volumes. The volume of the solution should be kept as little as possible. This is then heated on a water-bath for about five minutes, and after the addition of 2-3 g. of potassium iodide again heated on the water-bath for 10-15 minutes and cooled under tap water. A few c.c. (1-2) of starch solution were added and the blue colour was just discharged by the dropwise addition of a decinormal solution of sodium thiosulphate. An excess of sodium bicarbonate was then added to the solution slowly with stirring, diluted to 200 c.c. and titrated with a standard solution of iodine. If during transference of the bismuth phenylarsonate a large quantity of water be added, that should be evaporated to dryness and then equal volumes of hydrochloric acid and water should be added. For calculation : 1 Bi $\equiv$ 1 As $\equiv I_2 \equiv$ 2 thiosulphate or 1 c.c. of $N/10$ iodine solution $=$ 0·01045 g. Bi.

Results

Bi taken.	Conc. HCl.	I_2 soln. (0·0999N)	Bi found.	Bi taken.	Conc. HCl.	I_2 soln. (0·0999 $N/10$)	Bi found.
0·02243 g.	2 c.c.	2·15 c.c.	0·02245 g.	0·1262 g.	6 c.c.	12·1 c.c.	0·1263 g.
0·0504	4	4·85	0·0506	0·1512	8	14·45	0·1509
0·0504	4	4·81	0·0502	0·0209	2	2·0	0·0209
0·0756	6	7·25	0·0757	0·0418	6	4·0	0·0418
0·1008	6	9·65	0·1007				

Concentrated hydrochloric acid, sodium bicarbonate, potassium iodide etc., used were all of 'pro analyse' variety of Kahlbaum.

Thus bismuth can be estimated volumetrically in presence of a number of elements, by the reagent phenylarsonic acid.

Micro-estimation of bismuth with this reagent is in progress.

My best thanks are due to Prof. P. Rây, for the facilities received in working out this piece of work in his laboratory.

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Calcutta

Received April 17, 1944.

ESTIMATION OF BISMUTH. PART IV. MICRO-ANALYSIS WITH PHENYLARSONIC ACID

By Anil Kumar Majumdar

A micro determination of bismuth, gravimetrically with phenylarsonic acid in presence of Ag, Hg (ic), Pb, Cu, Cd, Co, Ni Th (ous), alkalis, alkaline earths and sulphate ions, has been described.

The procedures are similar to those used in parts I and III of this series

In Parts I and III of this series, (*J. Indian Chem. Soc.*, 1944, **21**, 119, 187) it has been shown by the author that macro-quantities of bismuth can be estimated gravimetrically and volumetrically with the reagent phenylarsonic acid and separated from ilver, copper, cadmium cobalt, nickel, mercury (*ic*), lead, zirconium, thorium, tin, alkalis, alkaline earths (*e.g.*, Ca, Sr, Ba and Mg), thallium (ous) and sulphate ions.

The present paper deals with the estimation of small quantities of bismuth and its separation from copper, cadmium, cobalt, nickel, silver, mercury (*ic*), lead, alkalis, alkaline earths, thallium (ous)and sulphate ions.

During this investigation it has been found that the bismuth precipitate, obtained in presence of ammonium acetate, is of more crystalline character than what is obtained in presence of sodium acetate.

Bismuth is precipitated in a micro-beaker and by means of Emich's asbestos packed filter-stick, the filtration and washings are carried out. The beaker and the filter-stick containing the precipitate are dried in Benedetti-Pichler's drying apparatus in a current of dry air and weighed in a Kuhlmann's balance.

Experimental

The reagents and the standard solutions, used during this investigation, are exactly the same as were used earlier (Parts I and III of this series), except that instead of 10% solution of sodium or ammonium acetate, 20% solutions are used and that the bismuth nitrate solution, prepared from 'reagent quality' subnitrate and standardised in the same way as referred to in Parts I and III, containing only 0·997 mg. of bismuth per c.c., is taken.

Procedure.—During the micro-estimations almost the same procedures are followed as were described for the macro-method (*loc. cit.*).

For the estimation of bismuth, a measured quantity of the bismuth nitrate solution (containing just sufficient nitric acid to keep the bismuth in solution), from a micro-burette, was taken in a micro-beaker. To this solution were added 1 c.c. of the reagent solution (1% in water) and a few c.c. (2 to 3 c.c.) of the sodium acetate solution (20% in water) or after the addition of the reagent, the solution was just neutralised with dilute 2*N*-ammonia (using a drop of Wesselow's indicator), acidified with acetic acid (2*N*), 2 to 4 drops of which were added in excess and treated with 1 c.c. of ammonium acetate solution (20% in water). The solution was then diluted to 6-7 c.c. and heated for about 10 to 15 minutes in its stand on the boiling water-bath till the precipitate became crystalline. The precipitate was allowed to settle and collect at one side of the beaker. The supernatant solution was then drawn off through the asbestos-mat filter-stick and the precipitate was sucked as dry as possible. It was washed four to five times using 3 to 4 c.c. of hot water each time. The beaker with the precipitate and the filter-stick was first heated on the water-bath for about 10 minutes to remove all the adhering water and then finally dried for 20 minutes in a current of dry air at 100° in a Benedetti-Pichler's drying apparatus. The beaker with the precipitate and the filter-stick was then weighed in the micro-

balance after taking the usual precautions of wiping with moist flannel and dry chamois respectively, as prescribed for micro-methods.

The amount of bismuth was found by multiplying the weight of the bismuth compound with the factor 0·4906. Some of the results appear in Table I.

TABLE I

Bi taken.	Wt. of Bi-Complex.	Bi found.	Bi taken	Wt. of Bi-Complex.	Bi found.	Bi taken.	Wt. of Bi-Complex.	Bi found.
In presence of sodium acetate			In presence of am acetate			In presence of am. acetate.		
0·997 mg	2·023 mg.	0·992 mg.	1·545	3·137	1·539	2·642	5·411	2·655
0·997 mg.	2·030 mg	0·996 mg.	1·097	2·227	1·093	2·094	4·300	2·109
1·097mg.	2·228 mg.	1·093 mg.	0·598	1·210	0·594			
0·997	2·028	0·995						

If thallium (ous), alkalis and alkaline earth salts (*e.g.*, salts of Ca, Sr, Ba and Mg) are present in the solution, they do not interfere with the estimation of bismuth by the procedure given above.

It must be noted that large excess of sodium or ammonium acetate or prolonged boiling with excess of sodium or ammonium acetate leads to low results.

Estimation of Bismuth in presence of Sulphate ions.—To the solution, containing a few drops of dilute nitric acid in excess to keep the sulphate in solution, was added 1 c.c. of the reagent solution. If any precipitate appears, that should be dissolved with a few drops of dilute nitric acid and warming on the water-bath. The solution was then neutralised with dilute $2N$ ammonia (using a drop of Wesselow's indicator), acidified with acetic acid ($2N$), added 2 to 4 drops of acetic acid ($2N$) in excess, 1 c.c. of ammonium acetate solution and proceeded as usual. Results are given in Table II.

TABLE II

Bi taken	Sodium sulphate taken	Bi found	Bi taken	Sodium sulphate taken	Bi found
0 997 mg.	10·0 mg.	0·994 mg.	1·097 mg.	10·0 mg.	1·10 mg.

Estimation of Bismuth in presence of Copper, Cadmium, Silver, Cobalt and Nickel.—The nitrate solution, after the addition of 1 c.c. of the reagent, was neutralised with dilute $2N$-ammonia. A few crystals of potassium cyanide (reagent quality), sufficient to keep the interfering cations in solution, were then added, the solution acidified with $2N$ acetic acid solution (with a drop of Wesselow's indicator), 4 drops of acetic acid ($2N$) then added in excess along with 0·5 c.c. of the ammonium acetate solution, diluted to 6-7 c.c. and the usual procedure followed. Results are shown in Table III.

TABLE III

Bi taken.	Other metals taken.	Bi found.	Bi taken.	Other metals taken.	Bi found.	Bi taken.	Other metals taken.	Bi found.
0·997 mg	Cu 10·35	0·992 mg	1·097 mg	Cu 10·35	1·106 mg	1 296 mg	Cd 7·189	1·289 mg
1·097	Cd 7·189	1·091	0·997	Ag 10·61	0·994	0·997	Ag 10·61	0·991
0·997	Co 10·32	1·001	1·097	Co 10·32	1·099	1·097	Ni 12·06	1·104
0·997	Ni 12·06	1·001						

Estimation of Bismuth in presence of Lead.—In presence of lead, bismuth was estimated by the method followed for the individual estimation of it in presence of acetic acid buffered

with ammonium acetate except that after acidification of the solution with dilute acetic acid ($2N$) and addition of 4 drops of the acetic acid ($2N$) in excess, the solution was diluted to 6 c.c. and heated for some time on the water-bath with the addition of 0·5 c.c. of the ammonium acetate solution. If the precipitate was not crystalline, further quantities of the ammonium acetate solution, 0·5 c.c. each time, should be added and heated till the precipitate became so. The precipitate was then allowed to settle and treated as usual. Some of the results appear in Table IV.

TABLE IV

	Taken.	Ammonium acetate soln.	Bi found.		Taken.	Ammonium acetate soln.	Bi found.
Bismuth	1·047mg.	1 c.c.	1·052mg.	Bismuth	1·106mg.	1 c.c.	1·202mg.
Lead	14·24			Lead	7·12		

Estimation of Bismuth in presence of Mercury (ic).—To the nitrate solution (containing a little free nitric acid) was added 1 c.c. of the reagent and diluted to about 6 c.c., 0·5 c.c. of the ammonium acetate solution were then added and heated on a water-bath for some time. If the precipitate be not crystalline further portions of the ammonium acetate solution (0·5 c.c. each time) should be added and heated till the precipitate becomes crystalline. The precipitate was then allowed to settle and the usual procedure followed. Results as shown in Table V.

TABLE V

	Taken	Ammonium acetate soln.	Bi found.		Taken.	Ammonium acetate soln.	Bi found.
Bismuth	0·997mg.	1 c.c.	0·998mg.	Bismuth	0·997	1 c.c.	0·994
Mercury	10·06			Mercury	10·06		

My best thanks are due to Prof. P. Rây for the facilities received in working out this piece of work in his laboratory.

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COAGULATION STUDIES OF THE LATEX OF *CRYPTOSTEGIA GRANDIFLORA*, *R. BR.*—A WAR TIME SOURCE OF VEGETABLE RUBBER. PART I

By Rafat Husain Siddiqui, S. A. Warsi* and V. V. K. Sastri*

Studies on the coagulation of the latex of *Cryptostegia grandiflora* have been made with special reference to the hydrogen-ion concentration and the present paper embodies the results of auto-coagulation, auto-creaming, coagulation by heat, centrifuging, electric current, and water and those obtained by the action of chemical reagents on latex, e.g. mineral and organic acids, alkalis, bases, salts, reagents for coagulating proteins, hydration, dehydration and miscellaneous reagents like formaldehyde, lemon juice, curd and molasses. The observations show that rubber could be separated from the latex by the methods which are chemical as well as physical in nature.

The work was undertaken at the request from the Department of Supply with a view to evolving a method which would not require heavy expenditure of chemicals and will be workable by the same equipment used as in the case of *Hevea*.

With these objects in view the information has been collected with special reference to the hydrogen-ion concentration of the latex. The details of the methods are given in the experimental procedure.

Coagulation by Chemical Reagents.—Under this head are described the results of mineral and organic acids, alkalis, organic bases and salts and also special chemical reagents used for coagulating proteins and those which bring about hydration and dehydration. It is found that acids can coagulate the latex in a range which would require very small quantity of the coagulant and with an increase in acidity the percentage of coagulum would decrease. In most cases it is found that if the acidity reaches the limit which would drop the p_H of the latex from 4·6 to 4·0, the latex will not coagulate. Thus with a decrease of 0·6 in the value of p_H the latex is stabilised. Mineral and organic acids appear to be equally good and the coagulum produced has a good tensile strength and elasticity and can be sheeted. Organic acids from formic to butyric acid with an increase in the number of carbon atoms had no special advantage. The minimum quantities of acids, effective to coagulate a litre of latex, are given in Tables I and VIII ("The Science of Rubber" Eng. Ed., 1934, by Prof. K. Memmler, Translated by Dunbrook and Morris, New York, p. 121, 1934; P. Schidrowitz, "Rubber Recueil", 370**).

TABLE I

Coagulating effect of various substances

Coagulant.	Quantities per litre of 30% latex of Hevea with name of authors.				Quantities per litre of 2-7% of *Cryptostegia* latex by Siddiqui.
	Eaton.	Morgan.	Parkin.	Beadle & Stevens.	
Acetic acid	1·0 g.	1·0 g.	9·5 g.	1·5—6·0 g.	0·25—4 c.c.
Formic acid	0·6	0·8	4·5	...	0·25—2
Hydrochloric acid	0·7	0·7	1·0	0·4—0·5	0·25—1
Hydrofluoric acid	0·5	0·5	...	...	0·5—2
Nitric acid	1·0	1·0	3·0	...	0·1—0·2
Sulphuric acid	0·9	1·0	1·0	0·5—10	0·5—0·4
Calcium chloride	5·0	5·0	...	...	0·05—0·25 g.
Ammonium sulphate	10·0	10·0	...	...	0·05—0·25
Tannic acid	1·0	1·0	...	...	1·0
Oxalic acid	2·0	...	...	...	0·5—1·2
Tartaric acid	2·5	...	...	...	0·5—2
Citric acid	5·0	...	...	...	0·5—2

* Results embodied in Table III were done in collaboration with S. A. W. and V. V. K. S.

** References in this investigation are given of allied work of coagulation of the latices of *Manihot*, *Ficus*, Kickxia, Castilla, Hancornia, Mascarenhasia, Lianas (Vines), Euphorbia, Jelutong but with special reference to the work of *Hevea brasiliensis*.

When coagulation is effected with alkalis a minimum quantity of the reagent is necessary which would raise the p_H to 7·7. If the concentration is less there will be a partial coagulation and if it is more, the latex would turn into a pasty mass. In coagulation with alkalis there is an advantage that the process can be completed in a very short time but in the case of acids it is necessary to keep the latex overnight. The alkali coagulation has demerits as well. The coagulum is very spongy having a poor tensile strength and elasticity as compared to the coagulum obtained by acid coagulation. Further, the coagulum develops tackiness * and this depends further upon washing and temperature. If the coagulum is washed till it is free of of its alkalinity and is dried at low temperature (70-80°), the tackiness becomes less. This faulty coagulation can be corrected to a great extent if the coagulum is dipped in an 1% solution of mineral and organic acids before washing.

With bases (quinoline, aniline, toluidine and pyridine) it was found that 0·2 to 1 c.c. of the base brought about effective coagulation of 10 c.c. latex. Smaller quantities of quinoline, aniline and toluidine could not be used owing to the immiscibility of the bases with water. It was studied with pyridine only and it was noticed that 1 c.c. of 0·5% solution of pyridine in tap water coagulated 10 c.c. of latex. The coagula emit an odour of the base which is not removed even on washing with water and alcohol. The p_H value of the serum obtained after coagulation with bases could not be determined but with 0·5% solution of pyridine there was a gradual increase from 4·6 to 5·4 on increasing the volume of coagulant from 1 c.c. to 10 c.c. In the case of alkalis it was pointed out that with increased alkalinity the latex turned into a pasty mass but with bases this behaviour was not noticed.

The action of acids and alkalis on latex shows that the latex has got a stability range from 4·2 to 7·5 or 7·7. At the extremes complete coagulation of the latex takes place but below 4·0 the latex passes into a second zone or phase. The findings that alkalis are to be avoided for coagulation find further support from a statement of Stevens and Stevens "As a rule caustic soda should be avoided for latex manipulation as under certain conditions the resulting rubber tends to soften and becomes tacky (sticky) due to some obscure type of chemical decomposition."

The salts can be used for the coagulation of latex and very small quantities are required. Good results were obtained with calcium and sodium chlorides, aluminium and amonium sulphates and alum.

* Parkin, *Roy. Botn. Gard. Ceylon, Circ.* 1899, **1**, 151.

Eaton, *Dept. Agr. Federated Malay States, Sp. Bull.*, 1912, **17**, 25.

Zimmermann, "Dermanihot-Kautschuk," p. 250; G. Fischer, *Jrna*, 1913.

Ahrens, *Chem. Ztg.*, 1910, **34**, 266.

Gorter, *Dep Land. Nijverh en Handel, Medeel, over Rubber*, 1911, **1**, 4; 1912, **2**, 201.

Henri, *Caoutchouc and Gutta percha*, 1910, **7**, 4371.

P. Schidrowitz, "Rubber," 2nd. ed, 1916, p. 136.

O. de Vries, "Estate Rubber," p. 362.

Pohle, *Koll.-Chem. Beih.*, 1921, **13**, 32.

Bamber, Lectures on India Rubber, by D. Spence, 1909, p. 201,

O. de Vries and Benmee-Nieuwland, *Arch. Rubber Cultuur*, 1927, **11**, 567; 1925, **9**, 760.

Stevens and Stevens, "Rubber Latex," 1940, p. 16.

Flint, "The Chemistry and Technology of Rubber Latex", 1938, p. 167.

Weber, *Gummi. Ztg.*, 1904, **19**, 101.

A. W. de Jong and Tromp de Hass, *Ber.*, 1904, **37**, 3301.

Special coagulants for proteins were also used and they also coagulated the latex but the concentrations used in the experiments were not very effective and the coagula produced by picric and tannic acids were coloured. Alcohol and acetone alone also brought coagulation and the same result was achieved by common dehydrating agents.

Formaldehyde, lemon juice, curd, molasses and serum itself coagulated the latex and so shortages of chemicals is no consideration in the coagulation of latex.

Water Coagulation.—Coagulation can be effected by adding latex to six volumes of hot water while five volumes brought about partial coagulation and four volumes produced flocculation. The dilution varies from season to season with percentage of rubber; it is less when the percentage of rubber is high and more when it is less especially during the defoliation period. p_H value also depends upon dilution. If cold water is added dropwise till a clear straw coloured serum is obtained, the p_H rises to 7·5 but coagulation can also be brought about at low p_H value when six or seven volumes of hot water are used.

Auto-coagulation and Auto-creaming.—When latex is allowed to stand quietly at room temperature (25-31°) for a day or two the suspended particles float to the surface leaving below a clear reddish brown serum. This stage is characterised by the fact that particles do not coalesce together and on stirring or shaking disperse again in the serum. At this stage it is possible to separate the flocculated mass from the serum which can be made richer in rubber content and the particles of which can be coalesced together by washing with water or by filtration. When the latex is allowed to stand for a week or so at room temperature, the particles of cream unite together and form a clot of rubber having a junket-like appearance. Both of these methods can be used for the coagulation of latex on a large scale. The p_H value drops from 4·6 to 4·2.

Coagulation by Heat.—Latex can be coagulated by natural heat or by artificial heat (dry heat, moist heat and smoking). This process will have an important bearing if the whole rubber is to be obtained from the latex.

Coagulation by Centrifuging and Shaking.—This method can be used on a large scale. The coagulum gets separated and floats to the surface. A part of the coagulum remains in the serum which can be recovered on dilution. The p_H value of the latex remains unchanged.

Coagulation by Electric Current.—When the current from a battery is passed through the latex, the rubber particles move towards the anode and thus carry a negative charge and produce a change in the hydrogen-ion concentration of the latex. Observed p_H was 3·8.

By the above methods the coagulation of the latex of *Cryptostegia grandiflora* can be brought about. Broadly speaking the methods can be divided into two classes: (*i*) Chemical method which involves the use of chemicals and which are added to the latex either from outside (coagulation by chemical reagents and water, coagulation by smoking) or which are formed within the latex due to changes brought about by enzymes, micro-organisms, electric current or due to some unknown cause (auto-coagulation and coagulation by electric current). It is noticed that the chemical process is always accompanied by a change in the hydrogen-ion concentration which ranges from 4·2 to 7·5. (*ii*) Physical method which does not involve the use of chemicals (coagulation by dry heat, by centrifuging and shaking) and no change is brought about in the hydrogen-ion concentration of the latex.

Explanations for the coagulation of latex will form part of a separate communication.

EXPERIMENTAL

Coagulation by Chemical Reagents

(*a*) *General Methods of Coagulation with Acids and Salts.*—The latex is taken in a beaker, and required quantity of the acid or the salt solution added and the mixture warmed at 90° for five minutes after keeping overnight at room temperature (25-27°). The coagulum is separated, sheeted, washed well in running water, dried at 90-95° and weighed. This dry rubber is known as D. R. C. (dry rubber content).

(*b*) *General Method of Coagulation with Alkalis* (*Current Sci.*, 1943, p. 255) *and Bases.*—The latex is taken in a beaker On adding the required quantity of an alkali or an organic base the latex turns yellow or pink. The mixture is warmed for five minutes at 90°. On stirring with a glass rod a white coagulum and a clear yellow or reddish brown serum are obtained. The coagulum is sheeted and after washing well with water till it is free of alkalinity it is dried at 90-95° in an air-oven.

(c) *Difference between the Coagula obtained by the above two Methods.*—In the case of coagula obtained by method (*a*) the fibres of rubber unite together and from a tough and tenacious close meshed network. The texture is hard to feel and takes some time to sheet it. Its tensile strength is great and has good elasticity. The coagulum obtained by method (*b*) is of a different nature altogether. It is a highly spongy mass in which the mesh is open and the fibres or threads do not form one compact tough structure. The coagulum can be spread enormously but is extremely poor in tensile strength. It breaks easily and has poor elasticity.

Correction of the faulty Coagulation.—If the coagulum obtained by method (*b*) is washed and is given a dip in 1 % solutions of hydrochloric, sulphuric and acetic acids for 15 minutes, it acquires a white colour and resumes the tensile strength and elasticity. Before drying it should be washed well with water. On drying tackiness still persits to a slight extent.

Coagulation by Acids

Preliminary observations showed that increased acidity, which would decrease the p_H value of the latex from 4·6 to 4·0, would also decrease its percentage of dry rubber content (D.R.C., 111). This inference helped in fixing the concentration of the acid solution and the following was the procedure adopted. Prepare a dilute solution of the acid, add in portions of 1 c.c. to latex (10 c.c.) and note the p_H value after each addition till it reaches 4·0. If 1 c.c. of any solution decreases the p_H to 4·0, the acidity was considered very high and it was reduced to such an extent that 4 or 5 c.c. would at least be required to lower the p_H to 4·0. With most of the acids 1 % solution was found effective for coagulating the latex but hydrochloric, sulphuric, nitric and boric acids gave good results with 0·25, 0·2, 0·2 and 0·1% solutions respectively. After fixing the concentration of the acid solution its coagulating power was further studied by adding 1, 2, 3, 4, 5 and 6 c.c. to 6 portions of latex (10 c.c) and determining the D.R.C. The concentration of the solution was then halved and likewise five more determinations of D·R.C. were made. The range of acidity of the two solutions helped in deciding the minimum and maximum quantity of the coagulant that would bring about effective coagulation of the latex. In the following tables for each observation 10 c.c. of the latex were used and white coagulum was obtained which could be sheeted and had good tensile strength and elasticity. The indicator used was bromocresol green unless otherwise mentioned. D.R.C. values throughout this investigation are compared with D.R.C. obtained by coagulating an equal volume of latex with water

because it coagulates the latex completely as mentioned elsewhere and will be shown in the tables as standard. The solutions of the acids were prepared in tap water. Results appear in Table II.

TABLE IIA

Coagulating effect of inorganic acids

Hydrochloric acid

Hydrochloric Acid (Whitby, *Agr. Bull., Fed. Malay States*, 1918, **6**, 374) — With 0·5% solution two sets of experiments were done. In one the acid was mixed with latex and warmed in boiling water for 10 minutes and after keeping overnight was again warmed. In the second set the mixture was warmed only once after keeping overnight. It was found that warming after keeping overnight was better. It the first set of experiments there was flocculation but the flocks did not coalesce together. Experiments 1 and 2 gave coagula but in other cases increased acidity failed to produce any coagulum. From the second set it is clear that 1 c.c. of the acid solution containing 0·005 c.c. hydrochloric acid brought about coagulation of 10 c.c. latex to the extent of 94% and 0·025 c.c acidity decreased it to 15% Therefore the concentration of the acid solution was halved and 0·24% solution (2·5 c.c. concentrated acid in a litre of tap water) gave good results which showed that 0·025 c.c. of hydrochloric acid can bring about coagulation of 100 c.c latex. In the case of Hevea the required acidity is 0·04-0·05%.

	(a) With 0·5% solution Mixture warmed before and after keeping overnight: (First set.)			(b) With 0·5% solution. Mixture warmed only once after keeping overnight: (Second set.)			(c) With 0·25% solution		
Vol. of coagulant in c.c.	Appearance of serum.	p_H.	% of D.R.C. on vol. basis.	Appearance of serum.	p_H.	% of D.R.C. on vol. basis.	Appearance of serum.	p_H.	% of D.R.C. on vol. basis.
1	Milky	4·4	0·99	Turbid black	4·6	4·08	Dark and slightly turbid	4·4	4·76
2	,,	4·3	1·03	,,	4·4	3·97	,,	4·3	4·68
3	,,	4·2	0·53	Milky	4·3	0·30	,,	4·2	4·15
4	,,	4·1	0·82	,,	4·2	0·51	Milky	4·1	0·88
5	,,	4·0	0·65	,,	4·0	0·66	,,	4·0	—
6	,,	3·9	—	—	—	—	—	—	—
Standard	—	—	—	,,	—	4·46	—	—	4·91

Hydrobromic acid

(Best results are obtained with an acidity ranging from 0·005—0·003 c.c per 20 c.c. latex.)

	(a) With 1% solution.			(b) With 0·5% solution.		
1	Clear, deep dark	4·5	4·36	Clear, deep dark	4·5	4·27
2	,,	4·5	4·41	,,	4·5	4·41
3	,,	4·4	4·20	Turbid, deep dark	4·5	4·07
4	Turbid, deep dark	4·4	4·04	,,	4·5	3·84
5	,,	4·4	3·62	,,	4·5	3·76
6	,,	4·4	1·99	—	—	—
Standard	—	—	—	—	—	4·49

TABLE IIA (*contd.*)

Hydriodic acid

(Good reconéts are obtained with 0·005-0·030 c.c. acid per 10 c.c. latex)

Vol of coagulant in c.c.	(a) With 1% solution. Appearance of serum.	pH.	% D.R.C. on vol. basis.	(b) With 0·5% solution. Appearance of serum.	pH.	% D.R.C. on vol. basis.
1	Dark brown, turbid	4·4	2·12	Dark brown, turbid	4·4	4·50
2	,,	4·2	2·07	,,	4·4	4·37
3	,,	4·0	1·50	,,	4·3	4·32
4	Milky	—	—	,,	4·3	4·34
5	—	—	—	,,	4·2	4·13
Standard	—	—	—	—	—	4·49

Hydrofluoric acid

D. Sandmann, *Tropenflanzer*, 1910, 14, 189. F. Frank, *Gummi Ztg.*, 1908, 22, 1404.
(0·005-0·02 c.c. coagulated 10 c.c. latex effectively.)

	(a) With 1% solution.			(b) With 0·5% solution.		
1	Brownish red, turbid	4·4	6·83	Slightly milky	4·5	4·48
2	,,	4·2	6·69	Brownish red	4·4	6·95
3	Milky	4·1	—	,,	4·3	6·88
4	,,	4·0	—	,,	4·2	6·68
5	,,	4·0	—	Milky	4·1	3·84
Standard	—	—	—	—	—	6·89

Sulphuric acid

J. L. Wiltshire, *J. Research Inst. Malaya*, 1932, 4, 94. H. Jumelle, "les Plantes a Caoutchouc et a Gutta", p. 335, (Paris, 1932).

(Coagulant 0·005-004 c.c. per 10 c.c. latex while in the case of Hevea the acidity is 0·05-1·0%.)

	(a) With 0·2% solution.			(b) With 0·1% solution.		
1	Turbid, dark	4·4	4·57	Turbid, dark	4·4	3·94
2	,,	4·3	4·54	,,	4·4	3·90
3	Milky	4·2	0·97	,,	4·3	3·33
4	,,	4·0	0·15	,,	4·3	3·17
5	,,	—	0·15	,,	4·2	4·46
Standard	—	—	—	—	—	4·91

Nitric acid

(Coagulation was best effected with an acidity 0·001-0·004 c.c. per 10 c.c. latex.)

	(a) With 0·2% solution.			(b) With 0·1% solution.		
1	Turbid dark	4·3	3·75	Dark turbid	4·5	4·38
2	,,	,,	3·76	,,	,,	3·54
3	Milky	,,	2·35	,,	,,	3·42
4	,,	,,	2·72	,,	,,	2·95
5	,,	,,	1·54	,,	,,	3·19
Standard	—	—	—	—		4·89

Syrupy phosphoric acid

(The range of acidity necessary for coagulation was 0·005-0·01 c.c. per 10 c.c. latex.)

	(a) With 1% solution.			(b) With 0·5% solution.		
1	Turbid dark	4·1	4·18	Turbid dark	4·3	4·36
2	Milky	<4	2·14	,,	4·2	4·43
3	,,	,,	1·20	,,	—	4·30
4	,,	,,	0·11	Milky	—	0·24
5	,,	,,	0·07	,,	—	0·16
Standard	—	—	—	—	—	4·49

TABLE IIA (*contd.*)

Boric acid

(0·005-0·02 g. acid coagulated 10 c.c. latex. This coagulant with further has the advantage of preserving the coagulum.)

Vol. of coagulant in. c. c.	(a) With 0·1% solution. Appearance of serum.	p_H	% of D.R.C. on vol. basis.	(b) With 0·5% solution. Appearance of serum.	p_H	% of D.R.C. on vol. fasis.
1	Turbid	4·6	5·49	Brownish red and turbid	4·6	6·89
2	,,		6·57	,,		6·78
3	Milky	to	3·27	,,	to	6·51
4	,,		4·67	,,		6·50
5	,,	4·4	2·47	,,	4·4	5·75
Standard	—	—	—	—	—	6·15

Carbonic acid

[Air was blown by mouth into latex (10 c.c.) when a white coagulum and a very slightly turbid serum was obtained. The serum had p_H 4·2. The coagulum after usual working weighed 0·2660 g. (2·66%) while the standard weighed 0·2750 g. (2·75%). W. Pahl., 'The Rubber Industry,' Ed. by J. Torrey and A S. Wanders, p. 234, 1911. O. de Vries., 'Estate Rubber,' p. 187].

TABLE IIB

Coagulating effect of organic acids.

Acetic acid

[Stevens, *India Rubber J* 1955, 66, 521; Schdrowits and Goldsborough, *India Rubber World*, 1919, 44, 1147; Parkin, *India Rubber J.*, 1910, 40, 742; Crossbey, *ibid.*, 1911, 41, 1203; Morgan, "The Preparation of Plants Rubber," p. 58; "Plantation Rubber and Testing of Rubber," p. 44; Ultea, *Archief* 1217, 1, 407].

(0·1—0·4 c.c. of acid coagulated 200 c.c. of latex. Hevea latex requires 0·15—0·6% acidity.)

Vol. of coagulant in c.c.	(a) With 1% solution. Appearance of serum.	p_H	%of D.R.C. on vol. basis.	(b) With 0·5% soln. Appearance of serum.	p_H	%of D.R.C. on vol. basis.	(c) With 0·25% soln. Appearance of serum.	p_H	%of D R.C. on vol. basis.
1	Brownish red and turbid	4·4	5·46	Turbid	4·5	6·29	,,	4·6	6·66
2	,,	4·3	5·06	,,	4·4	4·45	,,	4·5	6·64
3	,,	4·3	5·37	,,	4·3	3·06	,,	4·4	3·97
4	,,	4·2	5·04	,,	4·2	4·13	,,	4·4	4·40
5	,,	4·1	3·88	,,	4·1	3·46	,,	4·3	4·50
6	Milky	4·0	0·37	,,	—	—	,,	—	—
Standard	—	—	—	—	—	—	,,		6·80

Oxalic acid

Vol. of coagulant in c.c.	(a) With 10% solution. Appearance of serum.	p_H	%of D.R.C. on vol. basis.	(b) With 0·5% solution. Appearance of serum.	p_H	%of D.R.C. on vol. basis.	(c) With 0·25% solution. Appearance of serum.	p_H	%of D.R.C. on vol. basis.
1	Dark	4·1	1·74	Dark brown	4·3	2·14	Clear, dark	4·5	2·15
2	Milky	4·0	0·24	,, ,,	4·2	2·15	,, ,,	4·4	1·55
3	,,	—	—	Milky	4·0	0·53	,, ,,	4·4	1·66
4	,,	—	—	,,	—	—	,, ,,	4·1	1·00
5	,,	—	—	,,	—	—	—	—	—
Standard	—	—	—	—	—	—	—	—	2·10

Results with acetic acid and oxalic acid solutions are presented in Table IIB. For mixtures with alcohol the followiug procedure was adopted. To latex (20 c.c.) were added 1 c.c. of 1% solution of acetic acid and 10 c.c. of alcohol drop by drop when there appeared a white coagulum and a reddish brown, turbid serum with p_H 4·6. The D.R.C. weighed 1·1986 g. (5·99%). Effect of alcohol was studied further. Observations are recorded in Table IIB.

Oxalic Acid, Acetic Acid and their Mixtures with Alcohol

In a previous communication (*J. Sci. Ind. Res.*, 1943, **2** 365), it was pointed out that acetic acid failed to coagulate the latex. That remark was due to the fact that coagulant was not added with special reference to the hydrogen-ion concentration and the quantity of acid added exceeded the minimum quantity required to coagulate the latex and hence the latex passed into a second phase in which it became stabilised. The coagulation of the latex of the second stabilised phase has not yet been studied.

TABLE IIc

Acetic acid and alcohol mixture

(a) With constant vol. of alcohol. Vol. of coagulant in c.c. 1% Acetic acid soln.	Alcohol.	Appearance of serum.	%of D.R.C. on vol. basis.	(b) With increased vol. of alcohol. Vol. of coagulant in c.c. %Acetic acid soln.	Alcohol.	Appearance of serum.	p_H.	%of D.R.C. on vol. basis.
1	4	Turbid reddish brown	5·17	1	2	Turbid	4·5	2*30
2	4	,,	4·62	2	4	,,	4·5	3*12
3	4	,,	4·38	3	6	,,	4·4	5*56
4	4	,,	3·10	3	8	,,	4·4	5*92
5	—	—	—	4	10	,,	4·4	6*18
6 standard	—	—	—	Standard	—	—	—	5*98

*The latex mixed with the coagulants was left overnight; dilution with the alcohol gave latter results.

TABLE IID

Coagulation with organic acids

Trichloroacetic acid

(0·01022-0·02044 g. was effective for coagulating 10 c.c. of latex).

Vol. of Coagulant in c.c.	Apearance of serum (a) With 1% solution	p_H	% D.R.C. on vol. basis	Appearance of serum (b) With 0·5% solution	p_H	% D.R.C. on vol. basis
1	Dark with slimy turbidity	4·3	5·37	Turbid	4·5	3·69
2	,, ,, ,,	4·2	3·78	,,	4·4	3·79
3	,, ,, ,,	4·01	1·62	,,	4·3	3·59
4	Thick, milky	—	0·53	,,	4·3	4·20
5	,, ,,	—	0·55	,,	4·2	3·84
6	,, ,,	—	0·32	—	—	—
Standard	—	—	—	—	—	4·93

TABLE IID (*contd.*)

Formic acid

[Spence, *India Rubber J.*, 1908, 425, Riebl, *Archief*, 1927 II, 354]. (Increased acidity decreased the percentage of rubber as observed in other cases. 0·03% Solution did not give good rasults)

Coagulant.	Serum.	p_H.	% D. R. C.	Serum.	p_H.	% D. R. C.
	(*a*) With 1% solution.			(*b*) With 0·5% solution.		
1 c.c.	Turbid	4·5	7·10	Turbid	4·5	4·00
2	,,	—	6·79	,,	—	4·24
3	,,	—	4·65	,,	—	4·48
4	Milky	—	2·66	Milky	—	2·47
5	,,	—	2·84	—	—	—
Standard	—	—	6·99	—	—	5·00

Butyric acid

(0·001—0·02 G. acid was found effective to coagulate 10 c c. latex. Increased acidity stabilised the latex.)

	(*a*) With 1% solution.			(*b*) With 0·5% solution.		
1	Dark and slimy turbidity	4·5	5·42	Dark and slimy turbidity	4.6	5·55
2	,, ,, ,,	4·5	4·91	,, ,, ,,	4·6	4·16
3	,, ,, ,,	4·4	4·59	,, ,, ,,	4·5	3·53
4	Milky	4·3	2·87	,, ,, ,,	4·5	2·44
5	,,	4·3	2·27	Milky	4·4	1 73
Standard	—	—	—	—	—	4·43

Tartaric acid

(0.01·0·03 G. acid coagulated 10 c.c. latex.)

	(*a*) With 1% solution.			(*b*) With 0·5% solution		
1	Dark brown	4·4	2·19	Turbid dark	4·5	1·75
2	,,	4·2	2·19	,,	4·4	1·62
3	,,	4·0	1·98	,,	4·2	2·00
4	Milky	—	0·93	Milky	4·0	0·73
5	,,	—	—	,,	—	0·72
Standard	—	—	—	—	—	2·00

Lactic acid

(An acidity of 0·005—0·03 brought about coogulation of 10 c c. latex.)

	(*a*) With 1% solution.			(*b*) With 0·5% solution.		
1	Dark, slimy turbidity	4·4	5·52	Dark, slimy turbidity	4·5	4·22
2	,, ,,	4·2	5·23	,, ,,	4·4	3·32
3	,, ,,	4·0	4·98	,, ,,	4·3	3·44
4	,, ,,	4·0	4·61	,, ,,	4·2	3·93
5	Thick, milky	—	0·96	,, ,,	4·1	4·42
6	,, ,,	—	1·16		—	—
Standard	—	—	—	—	—	5·06

Citric acid

(0·005-0 03 G. of the acid coagulated 10 c.c. latex.)

	(*a*) With 1% solution.			(*b*) With 0·5% solution.		
1	Turbid, dark	4·4	2 14	Turbid	4·5	2·18
2	,,	4·2	2·22	,,	4 4	1·87
3	,,	4·0	2·00	,,	4·2	1·71
4	,,	—	1·97	,,	4·0	1·71
5	,,	—	1·75	,,	—	1·53
6	,,	—	1·15	—	—	—
Standard	—	—	—	—	—	2·10

Stabilisation of Latex or its passing to the Second Phase (Whitby, *Kolloid Z.*, 1913 **12**, 156; O. de Vries and Beumeé-Nieuwland, *Arch. Rubber Cultuur*, 1926, **10**, 503).—If acid is added to the latex which would drop the p_H value to 4·0 then the latex will remain milky and will not coagulate and will pass into the second phase or zone (*cf.* Hevea). Latex (100 c.c.) was mixed with 0·5 c.c. of hydrochloric, nitric and sulphuric acids in separate corked bottles. On keeping for three months no coagulation occurred. Cream particles floated to the surface of the serum but they redispersed on shaking.

Coagulation with alkalis and organic bases

Alkalis.—In every case test experiments were done with alkalis. The solution of the alkali was added dropwise to the latex with stirring and on slight warming till a white coagulum separated from a yellow or reddish brown serum.

Organic Bases.—Base was added to 10 c.c. latex when coagula were obtained which emitted an odour of the base and had brown streaks. The coagula were washed with water and finally with alcohol but still the smell of the base persisted. Due to the immiscibility of the bases with water smaller quantities of the bases were not used excepting pyridine.

TABLE III

Coagulating effect of alkali and organic bases

Vol. of coagulant.	Appearance of serum.	p_H.	% of D. R. C. on vol. basis	Vol. coagulant	Appearance of serum	p_H.	% of D. R. C. on vol basis.
Lime water							
(For p_H values from 6·2 to 7·4 bromothymol blue and for 8·9 universal indicator were used)							
(*a*) With saturated lime water diluted in the ratio 10 : 19 (lime water : tap water)				(*b*) With saturated lime water diluted in the ratio 1 : 1 (lime water : tap water).			
10 c.c.	Milky	4·6	...	10 c.c.	Milky	5·2	2·23
20	,,	4·8	...	20	,,	6·2	2·40
30	,,	5·0	3·04	30	...	...	...
Standard	...	...	3·89	Standard	...	...	2·90
(*c*) With saturated lime water at 31°, (*N*/25·5 approximately).				(*d*) Coagulant after mixing and warming gave a precipitate.††			
10	Dirty	7·1	2·50	10	Pinkish, dirty	...	1·85
20	Clear red	7·2	3·70	20	Clear red	7·4	3·26
30	...	...	...	30	,, ,,	8·4	3·69
Standard	...	...	...	Standard	...	...	3·89
Potassium hydroxide							
(Bromothymol blue was used blue as indicator.)							
(*a*) With *N*/20 solution.				(*b*) With *N*/20 solution.			
10	Dirty light pink	7·2	1·69	20	Clear red	7·7	3·50
Standard	...	...	2·90	30	,,	...	3·30
				Standard	...	...	3·89

†† The percentage of the coagulum was reduced owing to the decrease in alkalinity.

TABLE III (*contd.*)

Sodium carbonate

(Bromothymol blue was used as an indicator)

Coagulant.	Serum	p_H.	% D. R. C.	Coagulant.	Serum.	p_H.	% D. R. C.
(*a*) With $N/20$ solution.				(*b*) With $N/20$ solution.			
10 c.c.	Dirty pink	6·5	1·69	30 c.c.	Clear red	7·7	3·65
20	,, ,,	7·5	1·80	Standard	...	...	3·89
Standard	...	...	2·90				

*Sodium hydroxide**

(Weber, *Ber.*, 1904 **37**, 3299. Bromothymol blue was used as an indicator).

10 of $N/20$ solution	Dirty pink	7·2	...	1 of *N*-soln.	Clear red	7·7	3·55
20 ,, ,,	Clear red	7·7	3·40	2·5 of *N* ,,	No coagulation, no separation of coagulation and serum on adding 2·5 c.c. more.		
20 of $N/10$ soln.	,, ,,	7·7	3·67				

* Slight variations in D. R. C. percentages are due to variation sampling.

Ammonium hydroxide

This is used for the preservation of Hevea latex. When added to the latex of *Cryptostegia* a big spongy clot of rubber separated which either turned black or developed black streaks on its upper surface and this observation pointed out that ammonia could as well be used as a coagulant.

(*a*) With 0·1% solution (0·1 c.c. of ammonia, in 100 c.c. water, $d = 0·88$.				(*b*) With 0 05% solution			
1 c c	Turbid	...	4·98	1	Turbid	...	4·41
2	,,	...	5·81	2	,,	...	2·68*
3	,,	...	3 10	3	,,	...	5·72
4	,,	...	5·36	Standard	,,	...	5·54

* The variations in the percentage of the coagula are probably due to the escape of ammonia from the mixture on warming and keeping.

Quinoline

(1 c.c. weighed 1·032 g. The coagula had brown streaks.)

0 2 c c.	Slightly turbid	...	7·66*	1·4	Slightly turbid	...	7·25
0·4	,,	...	7·60	1·6	,, ,,	...	7·06
0·8	,,	...	7·61	2·5	,, ,,	...	7·25
1·2	,,	...	7·60	Standard	,, ,,	...	6·56

* Variations may be due to washing and increased amount of the base which had no advantage.

Aniline

(Pelizzola, *Giorn Di Chim. Ind. ed. Appl.* **6**, p. 10.)

(1 C.c. weighed 1·021 g. The coagula were slightly coloured).

0·2 c.c.	Slightly turbid	...	6 90	1·4	Slightly turbid	...	6·67
0·6	,, ,,	...	7 05	1 8	,, ,,	...	6·65
1·2	,, ,,	...	6 00	Standard	...	...	6·56

TABLE III (*contd.*)

Coagulant.	Serum.	p_H	% D.R.C.	Coagulant.	Serum.	p_H.	% D. R. C

Aniline hydrochloride

The solution was prepared by dissolving 0·5 g. in 100 c.c. tap water. Small volume of 0·5% solution gave coagulum, but in most cases the serum remained milky. As this salt did not yield good results, salts of other bases were not used. (Th. Marx., *Tropenpflanzer*, 1912, **16**, 92).

1 c.c.	Turbid	...	5·69	4 c.c.	Milky	...	Nil*
3	,,	...	5·54	Standard	...	...	6·56

* Eleven experiments were done with the increased quantity of the coagulant, but none produced any coagulum after Expt. 3.

Toluidine

0·2	Slightly turbid	...	7·07	1·4	Slightly turbid	...	6·88
0·4	,, ,,	...	7·36	1·6	,, ,,	...	6·44
0·8	,, ,,	...	6·98	2·5	,, ,,	...	6·67
1·2	,, ,,	...	7·18	Standard	...	...	6·55

Pyridine

1 C.c. weighed 1·0206 g. The coagulum obtained from the bases (quinoline, aniline, toluidine and pyridine) is very spongy and can be sheeted enormously, but the texture is weak and has very little tensile strength as compared to the coagula obtained from acid coagulation. The experiments were performed by adding free base to the latex as well as by adding its solution in water. The coagula emitted pyridine smell and were white.

(a) With 1% solution.				(b) With 0·5% solution.			
0·2	Brownish red, turbid	...	6·52	1	Turbid	4·6	5·30
0·6	,, ,, ,,	...	6·60	3	,,	4·9	5·28
1·0	,, ,, ,,	...	6·46	5	,,	5·0	4·95
1·4	,, ,, ,,	...	6·70	9	,,	5·3	4·89
2·0	,, ,, ,,	...	6·86	10	,,	5·4	5·24
Standard	...	...	6·56	Standard	..	...	4·89

Coagulation by Salts

Very dilute solutions of salts were used firstly because latex gets coagulated with tap water which contains only small quantities of dissolved substances and secondly because large quantities, if used and found useful, will not be available on account of shortage of chemicals due to war. The hydrogen-ion concentration values were helpful as a guide to the coagulation point when water, acids and alkalis were used as coagulants, but they led to no definite information with most of the solutions of the salts used for coagulating the latex in this investigation. Extremely weak solutions of sodium and calcium chlorides, aluminium and ammonium sulphate and alum gave good results. In all these experiments 0·1 and 0·05% solutions of the salts were used.

TABLE IV

Coagulating effects of various salts.

Vol. of coagulant.	Appearance of serum.	p_H.	% of D. R.C. on vol. basis	Appearance of serum.	p_H.	% of D. R. C. on vol. basis.
			Alum *			
	Markley, *India Rubber Work*, 1908, **36**, 401. H P. Stevens, *R. G. A. Bull.* 1920, **2**, 142.					
	(a) With 0·05% solution.			(b) With 0·05 % solution		
1	Turbid	4·6	6·82	Turbid	4·6	7·30
2	,,		7·13	,,		6·75
3	Milky	to	4·89	,,	to	6·85
4	,,		5·09	,,		6·51
5	,,	4·7	5·79	,,	4·5	6·21
Standard	—	—	—	—	—	7·00

TABLE IV (*contd*).

Coagulant.	Serum.	pH.	% D. R. C.	Serum.	pH.	% D.R.C.
			Aluminium sulphate			
	(a) With 0·1 % solution.			(b) With 0·05 % Solution.		
1 c.c.	Turbid	4·6	5·78	Turbid	4·6	6·90
2	,,		4·12	,,	to	7·30
3	,,	to	3·40	,,		6·38
4	,,		3·90	,,		6·25
5	,,	4·5	3·40	,,	4·5	6·31
Standard	—	—	—	—	—	7·00
			Calcium chloride			
	(a) With 0·1 % solution.			(b) With 0·05 % solution.		
1	Turbid	4·6	7·60	Turbid	4·6	8·09*
2	,,		6·08	,,		7·16
3	,,		6·10	,,	to	6·86
4	,,	to	5·09	,,	4·5	6·41
5	,,		6·18	,,	—	—
6	,,	4·5	5·40	,,	—	—
Standard	—	—	—	—	—	6·89

A. Zimmermann, *Pflanzer* 1911, **7**, 409; G. Varnet, *Compt. rend.*, 1922, 175, 716; Lindet, *ibid.*, 1922, **176**, 798.

* Variations due to sampling. Sometimes cream comes on the top and if not properly shaken, will cause fluctuations in D. R. C.

Coagulant.	Serum.	pH.	% D. R. C.	Serum.	pH.	% D.R.C.
			Sodium chloride			
	(a) With c.1 % solution.			(b) With 0.05% solution.		
1	Milky	4·5	3·79	Turbid	4·5	7·15
2	Turbid	,,	6·32	,,	,,	6·68
3	,,	,,	6·03	,,	,,	5·97
4	,,	,,	5·94	,,	,,	6·18
5	,,	,,	6·10	—	—	—
Standard	—	—	—	—	—	—
			Ammonium sulphate			
	(a) With 0·1% solution.			(b) With 0·05% solution.		
1	Turbid	4·5	6·40	Turbid	4·5	6·21
2	,,	,,	6·24	,,	,,	5·78
3	,,	,,	5·16	,,	,,	6·40
4	,,	,,	5·99	,,	,,	5·80
5	,,	,,	5·71	,,	,,	6·01
Standard	—	—	—	—	—	6·89
			Aluminium chloride			
	(a) With 0·1% solution.			(b) With 0·05% solution.		
1	Turbid	4·4	6·08	Milky	4·5	3·51
2	,,		4·74	,,		3·52
3	,,		3·98	Turbid	,,	5·53
4	,,	to	4·04	,,	,,	5·07
5	Milky		1·50		,,	4·84
6	,,	4·3	2·71	—	—	—
Standard	—	—	—	—	—	6·89

TABLE IV (*contd.*)

Coagulant.	Serum.	p_H.	% D. R. C.	Serum.	p_H.	% D R.C.
			Mercuric chloride			
			Lecompte, *Ind. Rubber J.*, 1913, **46**, 19.			
	(*a*) With 0·1% solution.			(*b*) With 0·05% solution.		
1 c.c.	Turbid	4·5	6·19	Thick, milky	4·5	3·96
2	Thick, milky	,,	2·38	,,	,,	2·80
3	,,	,,	1·25	,,	,,	1·52
4	,,	,,	1·13	,,	,,	1·92
5	,,	,,	0·88	—	—	—
Standard	—	—	—	—	—	6·89
			Nickel sulphate			
	(*a*) With 0·1% solution.			(*b*) With 0·05% solution.		
1	Turbid	4·5	5·94	Turbid	4·5	4·65
2	,,	,,	5·65	,,	,,	5·67
3	,,	,,	5·38	Milky	,,	3·23
4	,,	,,	4·20	,,	,,	1·70
5	Milky	,,	3·00	—	—	—
Standard	—	—	—	—	—	6·89
			Cobalt nitrate			
	(*a*) With 0·1% solution.			(*b*) With 0·05% solution		
1	Milky	4·5	3·78	Milky	4·5	3·05
2	,,		3·10	,,		3·90
3	,,	to	3·84	,,		4·25
4	,,		2·99	,,	to	4·88
5	,,		3·83	,,	4·4	3·37
6	,,	4·4	3·03	—	—	—
Standard	—	—	—	—	—	6·89
			Lead acetate			
	(*a*) With 0·1% solution.			(*b*) With 0·05% solution.		
1	Turbid	4·5	4·28	Turbid	4·5	5·14
2	Milky		3·50	Milky	,,	3·55
3	,,		3·94	,,	,,	4·70
4	,,	to	3·96	,,	,,	2·26
5	,,		2·94	,,	,,	3·06
6	,,	4·3	3·52	,,	,,	—
Standard	—	—	—	—	—	6·89
			Copper sulphate			
			(Coagulum was brownish.)			
	(*a*) With 0·1% solution.			(*b*) With 0·05% solution.		
1	Turbid	4·4	6·40	Turbid	4·4	5·58
2	,,		6·41	,,		5·63
3	,,	to	5·05	,,	to	5·86
4	,,		4·59	,,		5·58
5	,,		2·03	,,	4·3	3·49
6	,,	4·3	3·59	—	—	—
Standard	—	—	—	—	—	6·89

TABLE IV (*contd.*)

Zinc chloride.

Coagulant.	(a) With 0·1% solution. Serum.	pH.	%D.R.C.	(b) With 0·05% solution. Serum.	pH.	%D.R.C.
1 c.c.	Milky	4·5	4·72	Milky	4·5	3·91
2	,,	,,	3·63	,,	,,	5·82
3	,,	,,	2·32	,,	,,	2·52
4	,,	,,	3·35	,,	,,	2·67
5	,,	,,	2·71	,,	,,	3·70
6	,,	,,	2·97	—	—	—
Standard	—	—	—	—	—	6·38

Manganese sulphate

	(a) With 0·1% solution.			(b) With 0·05% solution.		
1	Turbid	4·5	7·53	Turbid	4·5	7·37
2	,,	,,	5·52	,,	,,	7·41
3	,,	,,	4·95	,,	,,	7·03
4	,,	,,	5·01	,,	,,	6·78
5	,,	,,	4·99	,,	,,	6·86
6	Milky	,,	3·52	—	—	—
Standard	—	—	—	—	—	7·89

Potassium ferrocyanide

	(a) With 0·1% solution.			(b) With 0·05% solution.		
1	Slightly turbid	4·5	7·12	Turbid	4·5	5·62
2	,,	,,	7·22	,,	,,	5·76
3	Milky	,,	1·80	,,	,,	6·05
4	,,	,,	1·44	,,	,,	5·71
5	,,	,,	1·98	,,	,,	5·22
Standard	—	—	—	—	—	7·89

Potassium fericyanide

	(a) With 0·1% solution.			(b) With 0·05% solution.		
1	Turbid	4·5	7·35	Turbid	4·5	8·21
2	,,	,,	7·13	,,	,,	7·01
3	,,	,,	4·53	,,	,,	6·12
4	Milky	,,	3·56	,,	,,	7·38
5	,,	,,	3·76	,,	,,	5·21
Standard	—	—	—	—	—	7·89

Sodium silicofluoride

	(a) With 0·1% solution.			(b) With 0·05% solution.		
1	Milky	—	4·80	Turbid	—	5·87†
2	,,	—	2·30	Milky	—	2·73
3	,,	—	1·50	,,	—	3·21
4	,,	—	2·55	,,	—	2·11
5	,,	—	1·97	,,	—	3·61
Standard	—	—	1·92	—	—	7·89

† It appears that still lesser quantities of the coagulant will give better results

Coagulation and Hydration —Alcohol was used under this head and the details are given under reagents used for coagulating proteins.

Coagulation and Dehydration.—Anhydrous potassium carbonate, anhydrous sodium sulphate, sodium and potassium hydroxides, phosphorus pentoxide and zinc chloride were used. In every case 1 g. of the reagent was added to 10 c.c. of latex. Good and white coagulum was obtained with anhydrous sodium sulphate and zinc chloride, while a coloured coagulum was obtained with potassium carbonate. With potassium and sodium hydroxides pasty masses were produced. Phosphorus pentoxide thickened the latex.

Protein Coagulating Reagents. Alcohol (O. de Vries and Beumee-Nieuwland, *Arch. Rubber Culture*, 1927, **11**, 518).—98% Alcohol was gradually added dropwise to latex (20 c.c.) when on adding 11 c.c. a white coagulum and a turbid brownish red serum were obtained. The coagulum after sheeting weighed 1·2430 g. or 6·22%. The turbidity of the serum persisted even after adding a further volume of 13 c.c. of alcohol and appears to be due to the coagulated and separated proteins, etc. The p_H of the serum remained unchanged (4·6). Thus the volume of alcohol required to coagulate the latex is half the volume of latex taken for coagulation.

Acetone.—Acetone was added dropwise from a burette to latex (10 c.c.) when on adding 10 c.c. a white coagulum and a brownish red serum were obtained. The p_H value remained unchanged (Weber, *Ber.*, 1903, **36**, 3110; Schidrowitz and Kaye, *India Rubber J.*, 1907, **34**, 377).

Besides alcohol and acetone, picric, tannic, phosphotungstic acids were used for the coagulation of latex. The quantities of coagulants required to coagulate 10 c.c. latex were 0·05–0·1; 0·05–0·2; and 0·025–0·05 g. respectively. The coagulum from picric acid was yellow and from tannic acid violet, but it was white from phosphotungstic acid.

TABLE V

Coagulating effect of protein precipitating and miscellaneous reagents

Vol. of coagulant.	Appearence of serum.	p_H	% of D.R.C. on vol. basis.	Appearance of serum	p_H	% of D.R.C on vol basis.
			Picric acid			
	(*a*. With 1% solution.			(*b*) With 0·5% solution.		
1	Clear yellow	4·4	2·17	Clear yellow	4·5	2·17
2	Turbid yellow	4·2	1·70	,,	4·4	3·00
3	Deep yellow flocculation	4·2	—	Yellow flocculation	4·4	1·62
4	,, ,,	4·0	—	,, ,,	4·3	0·37
5	,, ,,	—	—	,, ,,	4·3	—
Standard		—	2·00		—	4·49

Tannic acid

Eaton, *Dept. Agr. Federated Malay States, Sp. Bull*, 1912, No. **17**, 17.

Vol. of coagulant.	Appearance of serum.	p_H	% of D.R.C. on vol. basis.	Appearance of serum	p_H	% of D.R.C on vol basis.
	(*a*) With 1% solution.			(*b*) With 0·5% solution.		
1	Dark violet, turbid	4·5	2·26	Dark violet, turbid	4·5	1·96
2	,, ,, ,,		2·05	,, ,, ,,		2·10
3	,, ,, ,,	to	1·89	,, ,, ,,	to	1·82
4	,, ,, Flocculation		0·43	,, ,, ,,		1·12
5	,, ,, ,,	4·3	0·68	,, ,, ,,	4·4	1·05
Standard		—	—		—	2·00*

* Latex was received at different intervals of time and hence the fluctuations in D. R. C.

TABLE V (*contd.*)

Phosphotungstic acid

Vol of coagulant.	Appearance of serum.	p_H	% of D.R.C on vol. basis	Vol. of coagulant	Appearance of serum	p_H	% of D.R.C. on vol. basis
	(*a*) With 1% solution.				(*b*) With 0·5% solution.		
1 c.c.	Flocculation	4·6	0·06		Dark Turbid	4·6	2·27
2	,,	4·5	0·21		,,	—	2·24
3	Turbid	4·4	2·25		,,	—	1·32
4	,,	4·3	3·00		,,	—	1·89
5	,,	4·3	3·47		,,	—	2·20
Standard		—	—			—	4·49

To latex (10 c.c.) was added with stirring 40 per cent formalin in portion of 0·1 c.c. A small pellet of rubber formed when 0·5 c.c. of the solution was added. Complete coagulation did not take place even after adding 1 c.c. but the latex thickened. On diluting the mixture with 50 c.c. water, flocculation occurred and the flocks formed the surface layer leaving below a clear layer of serum. On stirring, the flocks redistributed but did not coalesce together but stuck together after collection on a filter bed. The filtered mass was washed and dried in an air oven at 90-95° and weighed 0·5300 g. (5·30%). There was no change in the hydrogen-ion concentration of the serum before dilution. When this experiment failed, lesser concentrations were used and the results show that very dilute solutions of formaldehyde can bring about coagulation.

Formaldehyde

	(*a*) With 0·1% solution.			(*b*) With 0·05% solution.		
1	Brownish, turbid	—	7·03	Brownish, turbid	—	6·80
2	,,	—	6·36	,,	—	7·12
3	Milky, turbid	—	2·73	,,	—	6·64
4	,,	—	1·12	,,	—	6·02
5	,,	—	1·32	,,	—	1·58
Standard		—	—	—	—	6·89

Serum

Serum was added to latex and the mixture was kept in boiling water for 15 minutes but no change occurred in the p_H value. The results show that an increase in the volume of serum decreased the percentage of coagulum and accordingly lesser quantities of serum were used and gave better results.

5	Milky	4·6	5·02	2·5	Turbid	—	6·69
10	,,	,,	3·74	3·0	,,	—	5·89
20	,,	,,	0·10	3·5	,,	—	6·36
0·5	Turbid	—	6·89	4·0	,,	—	5·78
1·0	,,	—	6·85	4·5	,,	—	6·06
1·5	,,	—	7·21	5·0	,,	—	6·60
2·0	,,	—	7·27	5·5	,,	—	5·43
				Standard	—	—	6·89

*Lemon juice.**—(Wildeman, *J. L'Agric. Trop.*, 1905, 347) Latex (50 c.c.) was mixed with lemon juice (2 c.c.) which on keeping for 24 hours thickened but did not separate a coagulum, but on slight warming coagulated and the p_H value decreased from 5·0 to 4·5. The serum coagulated two further quantities of the latex.

*Curd.**—Sour curd was strained through muslin and 1 c.c. of this was added to latex (50 c.c.) The mixture thickened on keeping overnight and on stirring and gentle warming on the water-

* Note the p_H of latex and that of serum. The latex for these experiments was obtained last winter (January 1943).

bath separated into a coagulum and serum. The p_H dropped from 5·0 to 4·7. The serum coagulated two fresh quantities of latex more.

Molasses.—Thick molasses (2 c.c.) was added to latex (50 c.c.). On keeping overnight no change occurred in the consistency of the mixture but after stirring and warming on the water-bath for 15 minutes, the coagulum separated and the p_H value dropped from 5·0 to 4·5.

Coagulation by Addition of Water

Water was gradually added dropwise to latex (50 c.c.) and on addition of 20 volumes of water (1,000 c.c.) flocculation took place and the particles coalesced together to form a jelly-like spongy mass leaving behind a clear straw-coloured serum. The gelatinous mass on squeezing, pressing and washing formed a membrane which turned transparent on dehydration at 100°. The p_H values for distilled water, latex and serum were 7·0, 5·0 and 6·2 respectively. Latex of *C. grandiflora* can be coagulated with distilled water. (Dubosc and Luttringer, "Rubber: Its Production, Chemistry and Synthesis" Eng. Ed. by E. W. Lewis, 1918, p. 127 ; Siddiqui *et al., loc. cit.*).

The same behaviour is noticed by using tap water ; 12 to 16 volumes are necessary for complete coagulation and p_H values for tap water, latex and serum were 7·5, 5·0 and 7·5 respectively. But when the latex was diluted with water and warmed to 80-90°, the dilution was reduced to 8-10 volumes. If latex is added to boiling water, then the volume is further reduced to 6 and D.R.C. percentages of 3·8 and 3·5 were obtained when latex (10 c.c.) was coagulated with tap water (200 c.c. and 60 c.c. respectively), 5 volumes brought about partial coagulation while 4 volumes of water produced flocculation and the flocks did not agglomerate together even on keeping in boiling water but stuck together when collected on a filter and washed.

Fresh and saline waters from the Estate (Imperial Agricultural Research Institute Area) and river and canal waters were used and similar results were obtained. It may be pointed out that salinity decreased the extent of dilution while cold and ice-cold water had no advantage.

In the light of results of laboratory experience, the water coagulation method was developed and submitted to semi-large scale trials. A quantity of latex (6·5 lbs. was diluted with hot water ten times). The latex set to a spongy mass which formed a sheet $6\frac{1}{8} \times 4\frac{1}{4} \times 7\frac{1}{8}$ inches weighing $5\frac{1}{4}$ oz.

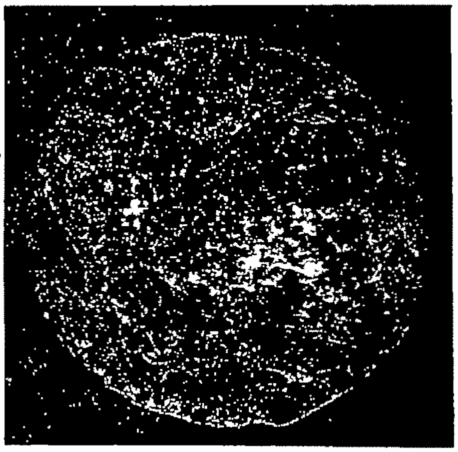
Formation of a Black Substance on Coagulation with Water.—When latex is coagulated with water and the coagulum and serum are allowed to stand overnight a black substance is formed over the coagulum as well as the serum. The liquid obtained from the pressings of the coagulum is also rich in it. (O. de Vries, "Estate Rubber" p. 30.) The black substance once developed on the coagulum is not removed on washing with water or acidulated water. Investigations on the cause of this revealed that alkalinity helps the formation of this black substance and acidity retards it (Zimmermann, *Pflanzer*, 1910, **6**, 117 ; D. Spence, *Gumni Ztg.* 1910, **22**, 1375). The coagulum after sheeting and washing if dipped for 15 minutes in 0·05% solution (acid 0·05 c.c. in tap water 100 c.c.) of hydrochloric, sulphuric and nitric acids remains white and can be kept under water exposed to the air without change in colour. The best results were obtained with nitric acid. The water is to be changed from day to day, otherwise it will develop a foul smell and bacteria. A sheet of rubber was kept immersed in water for two months after this treatment it remained white.

If the sheet is partially immersed in water, the portion exposed to the air becomes violet, brown and finally deepens in colour.

Auto-coagulation

When latex is allowed to stand for a few days at room temperature (28-30°) auto-coagulation results with the separation of a white spongy clot of rubber and a clear reddish brown serum having p_H value 4.2. In a previous communication (*J. Sci. Ind. Res.*, 1943, **2**, 357) the p_H was recorded as 4·6. The difference in acidity due to seasonal variations may be responsible for this). The coagulum when pressed into good sheets (Fig. 1) has good tensile strength and elasticity and does not show any properties of deterioration or decomposition. The auto-coagulation appears to be due to the changes of decomposition brought about by enzymes, ètc. present in the latex. An increase in the acidity and a shift of p_H value from 4·6 to 4·2 further confirms this observation. In some cases when the latex is allowed to stand quietly in uncorked bottles, the surface of latex turns violet-brown and finally black and on it develop moulds with a yellowish colour. The same moulds developed in the serum when it was exposed to air and were identified as (a) *Aspergillus flavus ovyzae* and (b) *Aspergillus niger van Teighen*. A sheet of undried rubber when kept in water without changing it and exposed to the air developed a foul smell and the examination showed bacteria (Vernet, *Bull. Marseille*, 1919, **1**, 118) and spores of saprophytic fungus like *Cladosperring Sp.* etc. Thus the change in auto-coagulation can be attributed to the action of enzymes, micro-organisms and also to some other unknown causes. (Gorter and Swart, *Meded. Rubber Profsta, Java* No. 6 ; D. spence, Lectures on India Rubber, 1909, 198).

FIG. 1



Auto-creaming.—When the latex is allowed to stand for a day or two its cream or suspended particles float to the surface leaving below a clear serum which can be syphoned off by a rubber tubing. The cream on separation forms a big clot of a spongy mass on dilution or washing with water. The cream also sticks by the agglomeration of particles when collected on a filter. This method is of practical importance and can be recommended for the coagulation of rubber and has the advantage that it requires less dilution for the coalescence of the rubber particles and also eliminates big coagulating equipment. (Flint, "The Chemistry and Technology of Rubber Latex" 1938, p. 167). The only necessary thing is to find a preservative so that it may not develop any bad smell due to decomposition on keeping, or when transported from place to place. This work will form part of a separate communication.

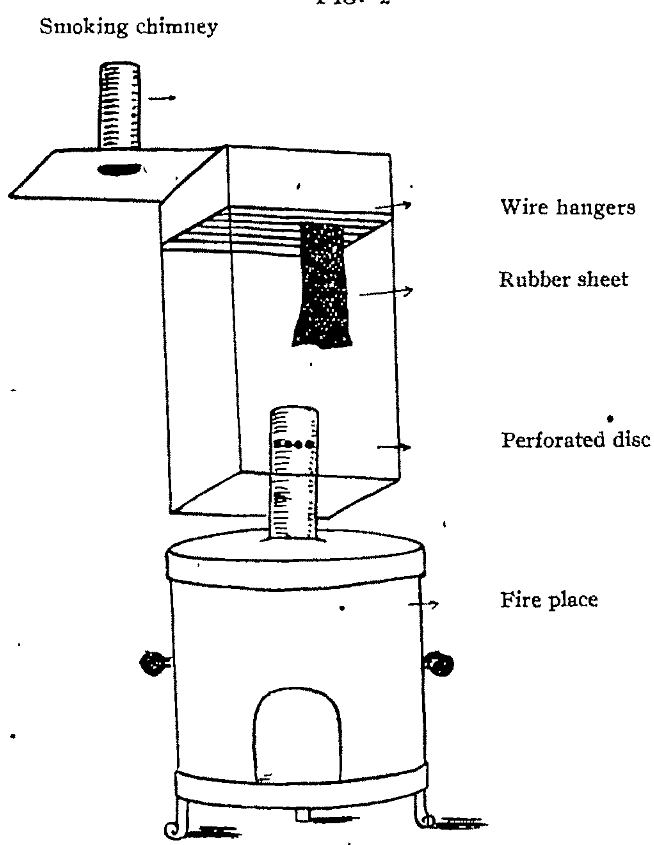
Coagulation by Heat

Natural Heat.—When a twig is cut the latex at the cut end dries up and forms a seal which can be pulled and the latex that flows down coagulates on the ground. Similarly when

the whip is scratched by a knife or a needle the small drops of latex ooze out and dry on it in small globules. These are examples of coagulation due to natural heat.

(*b*) *Artificial Heat. Dry Heat.*—When latex (10 c.c.) is warmed on a sand or water-bath, it begins to form a thin film or membrane on the upper surface of the latex at about 50°, then thickens and gradual and complete coagulation takes place at about 80 84° leaving a little brown serum (Duboc, and Luttringer, *loc. cit.*, p, 122). The p_H value of the latex remained unchanged (4·6). This process is important when whole rubber is required.

FIG. 2



Smoking.—When latex is exposed to the action of smoke then it gets concentrated and impregnated with smoke acids and cresote oil etc. The impregnation of the latex causes its coagulation. (Dominikos, *Gummi Ztg.* 1908, **22**, 926 ; G Waldrom, *India Rubber World*, 1906, **36**, 188). A smoking chamber designed in this laboratory is shown in Fig. 2. It consists of a fire-place and an upper chamber provided with a chimney and the arrangement for hanging rubber sheets. At the bottom the chamber is connected with the fire place with a perforated disc through which the smoke enters from the fire place to the upper chamber. The paddy husk was used in the fire place for producing smoke. Rubber sheets were also dried in this smoking chamber and suffered a loss of 31 and 17% on drying in three hours' time. The less moisture content in the second sheet may be due to good pressing. The sheet after drying appears to have properties of cured rubber and a strip cut from the sheet can be pulled four to five times its size and has a very good tensile strength and elasticity.

Moist Heat or Steam.—Steam was passed in a beaker containing latex (20 c.c.) for three minutes till the volume increased to 30 c.c. when a white coagulum and a turbid serum were obtained. The experiment was repeated thrice. The coagula after washing and drying at 90-95° gave 6·61, 5·90, 6·0%.

Coagulation by Centrifuging and Mechanical Shaking

Shaking.—Latex (10 c.c.) was shaken in a corked test tube till it separated into a coagulum and a clear straw coloured serum. The p_H value of the latex remained unchanged.

The D.R.C. amounted to 2·47% which was comparable to the percentage obtained by coagulating an equal volume of latex with water.

Centrifuging.—Latex (10 c.c.) was centrifuged in a rapidly rotating centrifuge when coagulum separated as a hard disc or button and came to the top within ten minutes. (D.R C. % of 4 observations were 5·5, 6·2, 6·3, 6·6). The serum was turbid and on dilution with water yielded a further quantity of coagulum. (D.R.C.% of 4 observations were 1·0, 0·6, 0·5 and 0·2). The p_H of the latex remained unchanged. This process can be used for the coagulation of latex on a large scale. (Biffen, *Kew. Bull. Misc. Information*, 1890, 179).

Separation of Coagulum from the Latex by Alpha-Alpha Separator.—A litre of latex was churned when a clear serum was obtained on feeding the latex a number of times. The coagulum stuck to the internal spherical balls and clogged the machine. The whole operation of the separation of coagulum was completed in ten minutes. This is also suggestive of the fact that a centrifuge used for sugar could be used for the separation of rubber from the latex on a large scale.

Coagulation by Electric Current

Current was passed through latex diluted with water by using copper electrodes when flocculation occurred but a clear serum was not obtained. The whole mass became dirty yellow and finally on keeping turned black. With carbon electrodes the serum as well as the coagulum did not turn black on passing the current. Finally the current was passed in a **U**-tube with platinum electrodes when the dispersed particles began to move towards the anode and bubbles began to come out copiously at the cathode at which there was also deposition of a substance which first turned yellow and finally from brown to black. The deposited matter at the anode even after keeping for a week remained white and came to the top in the limb of the **U**-tube leaving the clear serum below. The experiment indicates the charge carried by the dispersed particles of the latex to be negative. The p_H value of the serum was 3·8 and so the change is a chemical one brought about by the changes of decomposition which resulted in increased acidity of the serum. (*India Rubber World*, 1926, **75**, 127; *Trans. Inst. Rubber Ind.*, 1928, **4**, 343).

Stages of Coagulation. (Beadle and Stevens, *Kolloid, Z.*, 1913, **13**, 217).

1. *Formation and Separation of Cream.*—The latex is allowed to stand quietly at room temperature (25-31°) or when it is diluted with water (4 volumes) the fine suspended particles of latex slowly separate out and begin to float to the surface. If the liquid is stirred the particles again mix with the serum and redistribute uniformly to make it latex.

2. *Separation of Latex into Cream and clear Serum.*—The fine white particles of cream in (1) further agglomerate together and form bigger particles of cream and collect on the surface forming an upper surface of cream and lower layer of clear serum. The cream can be redistributed and separated by filtration.

3. *Coagulation.*—The upper white cream on touching with a glass rod forms a voluminous spongy and jelly-like mass due to the formation of a net-work of rubber threads and fibres by their crossings and recrossings and the whole clot can be lifted bodily from the serum. At this stage when the fine fibres or threads of rubber unite together they are no more particles of cream which can be redistributed in the serum on shaking or stirring. The cause has not been examined but it is probable that the change is brought about by the disruption of electrical and molecular cohesive forces.

Confirmation of the Results of Coagulation on a Semi-large Scale

The following coagulants were used to coagulate 1 pound of latex of *C. grandiflora* in order to confirm the results obtained by coagulating 10 c.c. of the latex. The following observations confirm the previous findings.

TABLE VI

Percentages of D.R.C. from 1 lb. latex

No.	Name of the coagulant.	Amount of the coagulant.	Vol. of water in which the coagulant wss dissolved	Wt. of D.R.C.	% of D.R.C. on wt. basis.
1	Hydrochloric acid	0·1075 c.c.	43 c.c.	24·69 g.	5·74
2	Nitric acid	0·043	43	23·76	5·54
3	Acetic acid	0·43	43	26·93	6·26
4	Sulphuric acid	0·172	43	28·59	6·65
5	Sodium hydroxide	0·43 g.	43	28·38	6·60
6	Ammonia (conc.)	0·86 c.c.	—	23·05	5·36
7	Pyridine	0·516	50	28·19	6·56

Cost of Coagulation.—Table VII shows the quantity of latex in lbs. which can be coagulated by one pound of the coagulant and its cost at present and pre-war rates and also the cost of coagulation of $9\frac{3}{8}$ tons of latex at present and pre war rates.

TABLE VII

Cost of coagulation

Name of coagulant.	Quantity of latex coagulated by 1 lb of coagulant	Price of coagulant.		Cost of coagulation of $9\frac{3}{8}$ tons of latex.	
		Pre-war rates.	Present rates.	Pre-war rates.	Present rates.
		Rs. As. P.	Rs. As. P.	Rs. As. P.	Rs. As. P.
Hydrochloric acid	3800 lbs	0 0 6	0 14 0	0 3 0	5 2 6
Sulphuric acid	1500	0 1 1	2 4 0	0 15 6	32 4 0
Nitric acid	9250	0 0 4	3 4 0	0 1 0	11 6 0
Sodium hydroxide	269	0 4 0	1 0 0	20 0 0	80 0 0
Boric acid	21500	0 5 6	3 8 0	0 5 6	3 8 0
Oxalic acid	2150	0 8 0	2 12 0	6 0 0	27 8 0
Citric acid	2150	1 2 0	12 8 0	11 4 0	125 0 0
Calcium chloride	21500	1 7 0	2 12 0	1 7 0	2 12 0
Sodium chloride	21500	0 10 0	1 2 0	0 10 0	1 2 0
Ammonium sulphate	21500	0 8 0	1 4 0	0 8 0	1 4 0
Aluminium sulphate	21500	1 6 0	5 8 0	1 6 0	5 8 0
Alum	21500	1 4 0	5 14 0	1 4 0	5 14 0
Acetic acid	200	0 10 0	3 15 0	67 3 0	416 0 0
Formic acid	300	1 10 0	....	116 7 0	....

TABLE VIII

Coagulating effect of various substances ††

Quantities of coagulants in g. or c.c. and water of dilution per litre of 2-7 % Latex of *Cryptostegia grandiflora*.

	Name of coagulant.	Coagulant in g. or c.c./litre		Vol. of water* in which the coagulant was dissolved	
		Minimum.	Maximum.	Minimum.	Maximum.
1.	Hydrochloric acid	0·25 c c.	1·0 c.c.	100 c.c.	400 c.c
2.	Hydrobromic acid	0 50	3·0	100	600
3	Hydriodic acid	0·50	3·0	100	600
4.	Hydrofluoric acid	0·50	2·0	100	400
5.	Sulphuric acid	0·40	0·5	100	200
6.	Nitric acid	0·10	0·2	100	200
7.	Phosphoric acid (syrupy)	0·5	1·0	100	200
8.	Boric acid	0·05 g.	0·3 g.	100	600
9.	Acetic acid	0·25 c.c.	4·0 c.c.	100	400
10.	Trichloracetic acid	0·5 g.	2·0 g.	100	400
11.	Formic acid	0·25 c.c.	2·0 c.c.	100	400
12	Butyric acid	0·5	3 0	100	600
13.	Tartaric acid	0·5 g.	1·2 g.	100	400
14.	Lactic acid	1·0 c.c	3·0 c.c.	100	600
15.	Oxalic acid	0·5 g.	1·2 g.	100	300
16.	Citric acid	0·5	2·0	100	400
17.	Lime water	10000 c.c. of $N/25·5$ solution		...	...
18.	Potassium hydroxide ‡	5·6 g.	5·6 g.	...	...
19.	Sodium carbonate ‡	11·0	11·0	...	...
20.	Sodium hydroxide ‡	4·0	4·0	...	...
21.	Quinoline †	20 c.c.	...	...	...
22.	Aniline †	20·0	...	...	...
23.	Toluidine †	20·0	...	...	...
24.	Pyridine	0·5	2·0	100	400
25.	Alum	0·05 g.	0·25	100	500
26.	Aluminium sulphate	0·05	0·25	100	500
27.	Calcium chloride	0·05	0·25	100	500
28.	Sodium chloride	0·05	0·20	100	400
29.	Ammonium sulphate	0·05	0·25	100	500
30	Aluminium chloride **	0 1	0·1	100	...
31.	Mercuric chloride **	0·1	0·1	100	...
32.	Nickel sulphate **	0·1	0·1	100	...
33.	Cobalt nitrate **	0·2	0·2	200	...
34.	Lead acetate	0·05	0·05	100	...
35.	Copper sulphate	0·05	0·20	100	...
36.	Zinc chloride **	0·1	0·1	100	...
37.	Manganese sulphate	0·05	0·25	100	500
38.	Potassium ferrocyanide	0·05	0.15	100	300
39.	Potassium ferricyanide	0·05	0·20	100	400
40.	Sodium silicofluoride	0·05	0 05	100	...
41.	Picric acid **	1·0	1·0	100	...
42.	Tannic acid **	1 0	1·0	100	...
43.	Lemon juice	40·0 c.c.	40·0 c c.	...	...
44.	Curd	20·0	20·0	...	...
45.	Water	6000	12000	...	...
46.	Formalin	0·05	0·2	100	400
47.	Alcohol (98 %)	555·0	555·0	...	...
48	Acetone	1000·0	1000	...	...

* No definite rule can be fixed for the minimum and maximum dilution. A concentrated solution would require lesser dilution. The table embodies the results of dilution found effective in this investigation.

‡ Dilution would depend upon the normality of the solution *e.g.* 1000 c c. lime water of $N/25·5$ strength are required to coagulate 1 litre of latex while only 10 c.c of 10 N-sodium hydroxide solution were effective

† Minimum and maximum quantities of the bases were not determined due to their immiscibility in water.

** Substances were not good coagulants in the concentrations used.

†† Coagulation studies embodied in this investigation were done mostly on latex having p_H 4·6 and collected from Okhla plantations, Delhi, during the months of August and September, 1943 and it was noticed that seasonal variations of temperature and time exercise a great effect in bringing about coogulation. Low temperature of winter months has a retarding effect while that of summer is favourable for it.

Practical Recommendations

The coagulation of *Cryptostegia grandiflora* latex can be brought about effectively by the following methods. The quantity of the coagulants required to coagulate one litre of latex are given in Table VIII and the details of the method in the experimental portion.

1. Water coagulation method.
2. Auto-coagulation method.
3. Auto-creaming method.
4. Coagulation by chemical reagents.
   (*a*) By mineral and organic acids.
   (*b*) By alkalis and pyridine.
   (*c*) Salts: sodium and calcium chlorides, aluminium and ammonium sulphates and alum.

CONCLUSIONS

1. Coagulation can be brougut about by methods which are physical and chemical in nature. The chemical methods are suitable for the coagulation of latex on a large scale.

2. The latex coagulates at a p_H range from 4·2-7·5.

3. The range towards p_H 4·2 is reached by acids and acid salts.

5. Coagulation when effected by chemical reagents, by auto-coagulation or by passing electric current is always accompanied by a change in the hydrogen-ion concentration of the latex.

6. Dilute solutions of alkalis, acids and of some salts give very good results.

7. If the quantity of the coagulant exceeds the minimum amount required for the coagulation of latex, no coagulation occurs and the latex passes into a second phase or zone.

8. When coagulation is effected by shaking, centrifuging, by the application of dry heat or by adding alcohol and acetone the p_H value of the latex remains unchanged.

9. Coagulation is also brought about by reagents used for hydration and dehydration and for precipitating proteins and also by micro-organisms and enzymes.

Our thanks are due to Mr. J. P. Anderson, Controller of Rubber, and Major H. R. Walden, Deputy Controller of Rubber and Officer-in-charge, Wild Rubber Section, Department of Supply, for the facilities and financial assistance for carrying out work on *Cryptostegia grandiflora* and other agricultural laticiferous plants in order to find out substitutes of *Hevea brasiliensis*.

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COAGULATION STUDIES OF THE LATEX OF *CRYPTOSTEGIA GRANDIFLORA*; R. Br. A WAR TIME SOURCE OF VEGETABLE RUBBER. PART II. EFFECT OF COAGULANTS ON THE QUALITY OF RUBBER

By Rafat Husain Siddiqui and M. L. Mathur *

A sample of latex has been coagulated with various coagulants. The coagula after extraction with alcohol, alcoholic potassium hydroxide and alcoholic hydrochloric acid have been analysed for proteins and ash. The observations show that the quality of rubber in general is not affected by a coagulant and 1/5 of resins, 1/7 of proteins and 1/9 of inorganic constituents originally present in latex remain adsorbed on rubber. An explanation of coagulation phenomena has been given.

The present investigation is the outcome of a previous communication (*J. Indian Chem. Soc.*, 1944, p. 191) which embodied results of coagulation of the latex of *Cryptostegia grandiflora* achieved by chemical (acids, alkalis, salts) and miscellaneous reagents, water, heat, electric current, mechanical stirring, auto-creaming and spontaneous or auto-coagulation and advanced some conclusions but reserved explanation about coagulation for a future report.

The present communication adduces arguments about the phenomena of coagulation and also describes the effects and changes produced in rubber when it is obtained by coagulating the latex with various coagulants.

A sample of latex on coagulation with coagulants gave percentages of dry rubber content (D.R.C.) ranging from 9·2-10·8, total solids, 18·4 and the serum solubles etc. as 7·6. The coagula were analysed for ash, total nitrogen, resins and rubber. They were next extracted with alcoholic potassium hydroxide and hydrochloric acid and in the unextracted residues ash and nitrogen were again estimated. It was found that the coagula did not show any further appreciable loss of resins, proteins and inorganic constituents after acid and alkali treatment. It was also evident from observations that the composition of rubber except in coagula obtained by auto-coagulation and cream (water) was more or less uniform and did not vary with the coagulants. Detailed examination of resins extracted from rubber is in progress and will form part of a separate communication.

The latex of *Cryptostegia grandiflora* is a milky white emulsion of minute globules suspended in an aqueous serum of complex composition while coagulation is a process of de-emulsification and resolution of latex into a coagulum and serum by agencies which may be physical and chemical in nature. The coagulum formed by the fusion of rubber with resins, proteins, and inorganic constituents has a spongy mesh work and is filled with serum but after its removal on pressing acquires a tough, tenacious and elastic structure. It has not been possible to obtain a coagulum consisting of pure rubber hydrocarbon by coagulants described in this investigation.

Number of theories have been advanced at times to explain the phenomena of coagulation. One postulates the phenomena to be due to the removal of protein (Weber, *Ber.*, 1903, **36**, 3108; Flamant, *Caoutchouc et la Guttapercha*, 1912, **9**, 6135; Hauser, 'Latex', New York, p. 91) or resin films (de Jong and Tromp-de Hass, *Ber.*, 1904, **37**, 3293). Coagulation is

* Only the ash and nitrogen determinations in this investigation have been done in collaboration with M. L. Mathur,

attributed by some to the action of enzymes (O de Vries, *India Rubber World*, 1924, **70**, 729) or bacterial activity (Corbet, *Bull. No.* I. *Rubber Res. Inst., Malaya*; Rhodes and Sekar, *J. Rubber Res. Inst. Malaya*, 1934, **6**, 176; Eaton and Grantham, *Agric. Bull. F. M. S.*, 1915-1916, IV, 26; Gorter and Swart, *Meded. Rubber Proefst., West Java*, 1916, **6**; de Vries, *Archief*, 1924, **8**, 333); while Gardner considers it a purely physical phenomenon caused by disturbance of the physical equilibrium of the latex (*Caoutchouc et la Gutta percha*, 1905, **2**, 351) and according to Kruyt (*Z. physikal. Chem.*, 1922, **100**, 250) latex is a lyophilic colloid of feeble solvation whose stability can be modified by electric charge and the solvation. "The particles of rubber carry a negative charge and if this be neutralised by the addition of acid or metallic ions, the solvation alone would be insufficient to assure stability of the system. In the same way, if in a latex of lightly charged particles the feeble solvation is nevertheless sufficient to produce stability, coagulation will result if the solvation be reduced by addition of dehydrating agent, *e.g.* alcohol or a conc. solution of caustic alkali." ("The Chemistry and Technology of Rubber Latex" by C. F. Flint, 1938, p. 114).

Our own observations show that coagulation of the latex of *Cryptostegia grandiflora* is brought about (*i*) by agents which coagulate proteins and which neutralise the charge on rubber particles, (*ii*) by hydration (water) and dehydration (anhydrous sodium sulphate, potassium carbonate, caustic alkali and alcohol), (*iii*) by auto-coagulation (enzymes and bacterial activity, (*iv*) by shaking, centrifuging, when the p_H remains unaltered, (*v*) by smoking, heat, electric current, etc.

The data further show that the rubber particles carry a negative charge and resins and proteins are not completely removed from the rubber but a portion remains adsorbed on it while another is eliminated during the process and is probably of a different nature. These observations lead us to share the views expressed by Kruyt and we think that coagulation is brought about on account of profound changes produced by physical and chemical agencies which destroy the stability of the system by partial or complete elimination of resins, proteins and serum constituents, neutralisation of charge on rubber and its separation as coagulum and by the disruption of electrical, molecular and cohesive forces that pervade latex of *Cryptostegia grandiflora*. We visualise a molecule of latex to be composed of a central core of rubber which is suspended in a stout bag of resins filled with serum and this bag is further enclosed in another bag made of proteinous matter, the intervening space being filled with serum. Internal changes due to enzymes etc. or the external to chemical or physical agencies make a puncture in the bags when the serum oozes out while the sac walls collapse and fuse with rubber. These fused particles on account of their lightness tend to rise to the surface of serum to form a dense layer of cream and it is by further fusion and coalescence of these cream particles that a spongy coagulum is produced during coagulation. Failure of coagulation or stabilisation of latex under certain conditions or at certain periods of its metabolism is probably due to an increase in tone and resistance of the films associated with rubber and the concentration of coagulants is not enough to overcome their protective action.

EXPERIMENTAL

A sample of latex obtained in the month of October, 1943, from Oakhla (Delhi) plantations having p_H, 4·6 was coagulated with various coagulants shown in Table I. For each coagulation 50 c.c. latex were taken and a coagulum was immediately obtained when alcohol, acetone, water, steam, sodium hydroxide were used as coagulants but with picric, acetic and mineral

acids and salt solutions the latex after mixing with the coagulant was kept overnight when it thickened and on warming and stirring with a glass rod for 2-10 minutes the flocks separated which soon coalesced together to a spongy white coagulum. The coagulum in each case after pressing and washing with water was kept dipped under water for two days. It was next kept in boiling water for half an hour. All the coagula were dried in an air-oven at 90°. When coagulation was effected with pyridine, alcohol and sodium hydroxide two volumes of latex were used. One coagulum from pyridine and sodium hydroxide was washed with water alone and the other was dipped in acetic acid (10%) before washing and they are shown in Table I as "pyridine (water), pyridine (acid), sodium hydroxide (water), sodium hydroxide (acid)". From alcohol coagulation one coagulum was removed at once from the serum while the other was allowed to remain in it overnight and they are shown in the table as 'alcohol I and alcohol II'. The serum had in some cases turbidity and from that of alcohol was analysed for nitrogen when it gave a value of 10·47 % (65·63 % as protein). Besides, one coagulum was obtained by centrifuging and another by spontaneous or auto-coagulation while the whole latex was secured by completely drying the latex to a constant weight at 90°. The total solids of one experiment are shown as cream (water) and for obtaining them latex (50 c.c.) was diluted with water (200 c.c.) when flocks separated which after removing from serum were dried at 90°.

TABLE I

% D. R. C. obtained by coagulating latex with various coagulants

No.	Name of coagulant.	Coagulant in c.c. or *g*.	Dilution with water.	Serum.	p_H	% D. R. C. on vol. basis.
1	Alcohol I	50 c.c.	...	Brownish with suspension	4·6	9·22
2	Alcohol II	50 c.c.	...	,, ,, ,,	4·6	10·07
3	Acetone	50 c.c.	...	,, ,, ,,	4·6	10·86
4	Picric acid	0·05 g.	5 c.c.	Yellow and turbid	...	10·34
5	Pyridine (water)	0·025 c.c.	,,	Slightly dark and turbid	5·0	10·50
6	Pyridine (acid)	0·025 c.c.	,,	,, ,, ,,	5·0	10·31
7	Sodium hydroxide (water)	*N*-soln.	,,	,, ,, ,,	...	10·23
8	Sodium hydroxide (acid)	,,	,,	,, ,, ,,	...	9·77
9	Acetic acid	0·25% soln.	,,	,, ,, ,,	4·2	10·37
10	Sulphuric acid	0·1% ,,	,,	,, ,, ,,	4·2	10·19
11	Nitric acid	0·1% ,,	,,	,, ,, ,,	4·2	10·27
12	Hydrochloric acid	0·25% ,,	,,	,, ,, ,,	4·2	10·36
13	Sodium chloride	0·05% ,,	,,	,, ,, ,,	4·5	9·83
14	Ammonium sulphate	,, ,,	,,	,, ,, ,,	4·4	10·25
15	Alum (potash)	,, ,,	,,	Brownish and turbid	4·5	10·62
16	Calcium chloride	,, ,,	,,	,, ,,	4·4	10·42
17	Aluminium sulphate	,, ,,	,,	Slightly dark and turbid	4·4	10·44
18	Pot. sulphate (anhd.)	5 g. ,,	,,	,, ,, ,,	4·5	10·43
19	Water (to complete coagulation).	...	...	Clear, straw coloured	..	9·80
20	Steam (till 130 c.c. condensed)	...	...	...	...	10·11
21	Cream (water)	...	200 c.c.	Straw coloured	...	10·20
22	Centrifuge (till coagulum separated).	...	...	Turbid	...	10·60
23	Auto-coagulation	...	...	Straw coloured	4·2	10·80
24	Whole latex	...	...	...	...	18·36*

* Total solids are on the weight of latex.

TABLE II

Composition of coagula

No.	Coagula from	Percentage composition of coagula.					Percentage composition of coagula. on latex						Percentage of substances removed with serum
		Ash	Nitrogen	Protein	Resins	Rubber	Moisture	Ash	Nitrogen	Protein.	Resins	Rubber	
1	Alcohol I	0·73	0·59	3·69	13·52	82·06	81·64	0·07	0·05	0·34	1·25	7·57	9·14
2	Alcohol II	0·84	0·69	4·29	13·37	81·50	81·64	0·08	0·08	0·43	1·35	8·21	8·29
3	Acetone	1·19	0·52	3·25	13·93	81·63	81·64	0·12	0·05	0·35	1·41	8·86	7·62
4	Picric acid	0·39	0·72	4·49	15·52	79·60	81·64	0·04	0·07	0·46	1·60	8·23	8·02
5	Pyridine (water)	0·39	0·68	4·23	14·29	81·09	81·64	0·04	0·07	0·44	1·50	8·51	8·61
6	Pyridine (acid)	0·14	0·68	4·26	13·40	82·28	81·64	0·01	0·07	0·44	1·38	8·47	8·05
7	Sodium hydroxide (water)	1·30	0·35	2·21	15·14	81·35	81·64	0·13	0·04	0·23	1·55	8·32	8·13
8	Sodium hydroxide (acid)	0·44	0·40	2·28	14·66	82·62	81·64	0·04	0·04	0·22	1·43	8·07	8·52
9	Acetic acid	0·25	0·58	3·64	13·39	82·72	81·64	0·03	0·06	0·38	1·39	8·57	8·00
10	Sulphuric acid	0·22	0·74	4·60	13·66	81·52	81·64	0·02	0·08	0·47	1·39	8·30	8·18
11	Nitric acid	0·18	0·64	4·01	13·99	81·82	81·64	0·02	0·07	0·41	1·44	8·39	8·10
12	Hydrochloric acid	0·35	0·76	4·74	14·12	80·79	81·64	0·04	0·08	0·49	1·46	8·29	8·08
13	Sodium chloride	0·30	0·55	3·45	13·55	82·70	81·64	0·03	0·06	0·40	1·33	8·13	8·53
14	Ammonium sulphate	0·71	0·65	4·04	12·59	82·66	81·64	0·07	0·07	0·41	1·29	8·47	8·11
15	Alum (Potash)	0·33	0·61	3·79	12·79	83·09	81·64	0·03	0·06	0·40	1·38	8·81	7·76
16	Calcium chloride	0·32	0·54	3·39	15·10	81·19	81·64	0·03	0·06	0·35	1·57	8·46	7·94
17	Aluminium sulphate	0·68	0·78	4·79	14·62	79·91	81·64	0·07	0·08	0·50	1·93	8·34	7·93
18	Sodium sulphate (anhydrous)	0·69	0·74	4·60	15·70	79·01	81·64	0·07	0·08	0·48	1·64	8·24	7·93
19	Water	0·30	0·60	3·72	14·19	81·79	81·64	0·03	0·06	0·37	1·39	8·04	8·55
20	Steam	0·52	0·77	4·77	13·55	81·16	81·64	0·05	0·08	0·48	1·37	8·20	8·26
21	Cream (water)	0·81	1·24	7·74	18·28	73·17	81·64	0·08	0·13	0·79	1·86	7·46	8·16
22	Centrifuge	1·16	0·78	4·90	14·20	79·75	81·64	0·13	0·09	0·53	1·55	8.68	7·47
23	Auto-coagulation	0·56	1·34	8·34	17·74	73·36	81·64	0·06	0·14	0·90	1·92	7·92	7·56
24	Whole latex *	3·55	2·12	13·26	36·31	46·88	81·64	0·65	0·29	2·43	6·67	8·61	...

The results given in Table I confirm our previous findings and show that there is not much of difference in the percentages of coagula obtained by coagulating the latex with various coagulants. They range between 9·2-10·8 thus showing a slight variationof 1·6% part of which may be due to sampling as it is difficult to maintain the uniformity of the sample. The total solids amount to 18·4% and the serum solubles or otherwise give a figure of 7·6%.

* Moisture has been assumed on the basis of loss suffered by latax on drying at 90°.

Under circumstances when the maximum difference in the percentages of coagula is 1·6 the water coagulation method seems to be the best as it does not require chemicals or keeping the latex overnight. The only difficulty of the process is that big coagulating pans would be necessary and to overcome this we think that cemented tanks of suitable size depending upon the daily supply of latex with an exit at the bottom would serve the purpose.

In order to find out the quality of rubber the coagula were analysed for ash, nitrogen and resins and rubber was calculated by difference. Table II embodies the results and percentage composition of coagula on the basis of D. R. C. and latex. Their ash was determined by heating them slowly and carefully in a platinum dish. Catching fire of combustible products was avoided. The material charred and finally a white ash was obtained. The nitrogen was determined by the method of Kjeldahl and to obtain a value for protein the percentage was multiplied by the factor 6·25. For the determination of resins coagula (not less than 1 g.) were extracted with alcohol four times (25 c. c. each time) on a water-bath for 20 hours. The alcoholic extract of coagula except that of whole latex and cream (water) was concentrated and on keeping at room temperature deposited a white substance, showing nitrogen 0·916 (5·73% as protein). The filtrate from this substance on removal of the solvent gave an ether-soluble oily residue (3·2516 g.) showing a nitrogen content of 0·485% while the ether-insoluble fraction was further resolved into water-soluble (0·0524 g.) having nitrogen 0·895% and water-insoluble (0·1 g.) with 1·964% nitrogen.

The foregoing table shows a high percentage of ash in coagula obtained from alcohol, acetone, sodium hydroxide, alum, ammonium and sodium sulphates and still higher in cream (water), centrifuge, auto-coagulation and whole latex but less in coagula from acid coagulants or those which were dipped in acid solutions before washing. Thus the ash content of total solids (whole latex) is 3·56% (0·66% on latex) while those of other coagula depend upon a coagulant. No generalisation can be made except that by coagulation ash-free rubber is not possible and that greater portion of the inorganic constituents is removed by serum and washing. Total nitrogen on the weight of whole latex is 2·12% (13·26% when calculated as proteins and 0·39% as nitrogen and 2·12% as protein on the weight of latex). Coagula from auto-coagulation and cream (water) show nitrogen 1·335 and 1·230% (8·34, 7·74% as protein) respectively and these values are higher than those obtained for other coagula which range from 0·35-0·77% (2·2-4·8% as protein). From the data it is evident that part of nitrogen is serum-soluble (14·9% as protein) and partly insoluble (8·3% as protein) and removal of a portion (3·5-6·1% as protein) from this depends upon coagulants. Turbidity of the serum in some cases and the analytical results of turbid mass obtained from serum after coagulating the latex with alcohol further supports this view point. The observed value for nitrogen was 10·47% (65·6% as protein). However, all the nitrogen cannot be proteinous and a considerable portion of it contained in the latex is removed during coagulation but 3-4% inspite of washings go into the mesh work structure of the coagula and probably continue to form shells surrounding the rubber particles. Comparative vulcanisation studies of whole latex and of coagula produced by auto-coagulation, water, acids, alkalis will decide the role of proteins in rubber.

The whole latex shows 36·31% alcohol solubles (resins) (6·7% on latex) while total solids from cream (water) and coagulum from auto-coagulation give 18·3 and 17·7% respectively. In other coagula the alcohol solubles range between 12·6-15·7%. Thus more than half of the resins are serum soluble and seem to be different from those which remain adsorbed on rubber by the formation of protective films which are not

removed at p_H 4·6-4·2. Rubber has been calculated by difference. The table further shows that in the total solids of *Cryptostegia grandiflora* resins, proteins and inorganic constituents which remain adsorbed on rubber amount to 1/5, 1/7, 1/6 respectively of those originally present in the latex.

It appeared however, necessary to find out whether the rubber hydrocarbon of coagula would show any further variation of percentage on extraction with alcoholic potassium hydroxide and alcoholic hydrochloric acid solutions.

TABLE III

Distribution of ash and nitrogen in coagula and their losses on extraction with EtOH-KOH and EtOH-HCl solutions

Coagula from	Loss after alc. KOH extraction %	Loss after alc. HCl extraction %	N after alc. extraction %	N after alc.KOH extran. %	N after alc.HCl extran. %	Ash after alc. extran %	Ach after alc.KOH extran. %	Ash after acl.KCl extractn %	Increase in ash after HCl extn. %
Group A Alcohol I, II, acetone, pyridine (water,) (acid), sodium chloride, acetic, sulphuric, nitric, hydrochloric acids, ammonium sulphate and alum (potash).	1·14	0·64 inc.	0·47 (avg. of 12 samples)	0·60	0·62	0·64 (avg. of 12)	0·79	0·71	
No. Group B.									
1. Calcium chloride	2·04	0·39 inc.	0·54	Not det.	0·49	0·32	Not det	0·57	0·25
2. Alumiuium sulphate	0·81	0·42 inc.	0·78	,,	0·82	0·68	,,	0·91	0·23
3. Sodium sulphate	3·57	No loss	0·74	,,	0·43	0·69	,,	1·17	0·48
4. Picric acid	0·12	0·35 inc.	0·72	,,	0·39	0·39	,,	0·80	0·41
5. Sodium hydroxide (water)	1·64	0·33 inc	0·36	,,	0·43	1·30	,,	1·25	—
6. Sodium hydroxide (acid)	0·07	0·23 dec.	0·40	,,	0·32	0·44	,,	0·76	0·32
7. Water	0·07	0·24 inc.	0·60	,,	0·43	0·30	,,	0·99	0·69
8. Steam	1·17	0·13 ,,	0·77	,,	0·74	0·52	,,	0·85	0·35
9. Cream (water)	2·32	2·34 ,,	1·24	,,	0·67	0·81	,,	1·26	0·45
10. Auto-coagulation	3·74	0·36 dec.	1·34	,,	1·02	0·56	,,	0·53	—
11. Whole latex	10·38	0·33 dec.	2·12	,,	0·17	3·55	,,	0·86	—

Extraction of the Coagula with Acoholic Potassium Hydroxide and Alcoholic Hydrochloric Acid Solutions.—The coagula were divided into two groups, A and B. The group A comprised 12 coagula while there were 11 in group B and were kept separate. The extraction was carried out with 0·5-*N*-alcoholic potassium hydroxide solution (100 c.c. for group A and 25 c.c. for each of the coagula of group B) The solution was prepared by dissolving potassium hydroxide (30 g.) in water (30 c.c.) and diluting the solution with alcohol (1000 c.c.) on the water-bath for six hours. The coagula were washed with alcohol and finally with water (twice) by warming on the water-bath for 6 hours. They were dried at 90° in an air oven and then in *vacuo* over sulphuric acid. Nitrogen and ash were determined for the coagula of group A only and the coagula of both the groups were next extracted with 0·5% alcoholic hydrochloric acid for six hours (30 c.c. for each sample of group B and 150 c.c. for

group A.) The coagula were washed with alcohol and finally with water and were dried as in the previous case. There was no loss of any significance by this treatment. There was a slight increase or decrease in weight. The coagula after extraction with potassium hydroxide solution showed losses which were more in those obtained from cream, steam and auto-coagulation, while the whole latex showed a loss of 10·4 %. The losses are due to the elimination of inorganic matter and proteins etc. as supported by data in Table III. The ash and nitrogen were determined in all the coagula of group A and B after their extraction with alcoholic hydrochloric acid and they required more sulphuric acid for digestion than it was ordinarily required in Kjeldahl estimation for nitrogen.

The foregoing table shows the course of nitrogen and ash in coagula after various treatments. In some cases there is an increase in the ash content and this corresponds with their increase in weight after alcoholic acid extraction. It is possible that some potassium hydroxide remained in rubber and combined with hydrohloric acid and the resultant potassium chloride adsorbed on rubber.

CONCLUSIONS

1. Whatever coagulant is used for coagulation a certain proportion of inorganic constituents, proteins and resins (1/9, 1/7, 1/5 respectively) of those originally present in latex remains adsorbed on rubber.

2. Half of the total solids are eliminated with serum during coagulation.

3. The quality of rubber does not vary with a coagulant.

4. The molecules of latex are sac like bodies consisting of an inner core of rubber surrounded by protective films of resins and proteins and the intervening spaces are filled with serum constituents. A puncture in the latex sac expels the serum constituents and brings about a collapse of the protective films which get adsorbed on rubber and these fused sacs float in serum as cream. It is by further fusion of cream particles that a spongy coagulum of rubber is produced.

5. Coagulation is brought about on account of profound changes in latex produced by physical and chemical agencies which destroy the stability of the system by elimination of resins, proteins and serum constituents, by the neutralisation of charge on rubber and by the disruption of electrical, molecular and cohesive forces that pervade latex.

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STUDIES IN ENZYMES. PART III. AMYLASES FROM SOME INDIAN TUBERS

By J. P. Shukla

Active diastatic enzyme occurs in (*a*) sweet potato, white variety (*Ipomoea batatas*) (*b*) Arvi (*Colocasia antiquorum*) (*c*) Banda (*Zingiber cassumunar*) and (*d*) Zimikand (*Amorphophallus campanulatus*).

The enzyme can be prepared by drying the material and taking the water extract of the dried meal followed by dialysis, precipitation with ammonium sulphate and alcohol and also by pressing the tubers and using the extracted juice for dialysis and precipitation. The extracted juice does not lose its amylolytic activity if preserved in cold under toluene.

The amylase occurring in sweet potato (white variety) resembles malt amylase and is saccharogen or β-amylase, whereas the amylase occurring in Arvi and Banda resembles the *Asp. oryzae* amylase and is α-amylase.

In a previous work the author (*J. Indian Chem. Soc.*, 1941, **18**, 407; 1942, **19**, 121) has studied the amylase from the tuberous root of the herb Kaseru (*Scirpus Grossus*, Linn). Amongst the tubers potato amylase has been very extensively investigated by many authors. Giri (*J. Indian Chem. Soc.* 1934, **11**, 339) extended the knowledge of a similar tuber-amylase by investigating the amylase occurring in sweet potato (red variety). Agarwal (*Proc. Indian Acad. Sci.*, 1937, **7**, 29; 1938, **8**, 384) found the presence of β-amylase in water chestnut (*Trapa bispinosa*, Roxb). The optimum p_H and temperatures of amylases from different sources differ to a very considerable extent. Recent work has shown (Kuhn, *Annalen*, 1925, **443**, 1) that there are two difinite types of amylases, α and β occurring in different sources.

Amylases have been finding increasing use in the industry and are extensively used in canning for clarifying jellies. In silk industry it is used for de-gumming, in paper and textiles it is applied for converting starch to a soluble form for de-sizing and is being sold under various trade names. Indirectly it is applied in brewing, and in the production of *miso* and *taka* diastase and in medicine.

In view of the increased demand for different amylases it would be only opportune to search out new raw materials whence this important enzyme can be tapped.

The present investigation relates to the presence of amylases in cheap raw materials extensively cultivated in India commonly as food vegetables. The commonly occurring tubers Arvi (*Colocasia antiquorum*), Banda (*Zingiber cassumunar*) and Zimikand (*Amorphophallus campanulatus*) have been investigated along with the sweet potato (*white variety*) and results compared with malt diastase prepared under similar conditions.

Experimental

Isolation and Detection of Amylase from the Tubers.—A bazar sample of the tubers was peeled and washed in water and softened in a mortar and pestle. The juice was expelled in a tincture press and preserved under toluene and tested for the presence of amylase by Linter method.

The figures in Table I indicate a definite presence of amylase in the juices extracted from the above tubers. It was possible to preserve the juices in the cold at 0°—4° under toluene for a period of one year without much loss in amylolytic activity except in the case of Zimikand.

TABLE I

Source.	Linter value.	Linter value after storing for one year at 0°.
Sweet potato extract (*Ipomoea batatas*)	130	125
Arvi extract (*Colocasia antiquorum*)	65	62
Banda extract (*Zingiber cassumunar*)	72	68
Zimikand extract (*Amorphophallus campanulatus*)	35	19
Germinated barley or malt extract	55	52

A more convenient method of preserving the enzyme was by converting the tubers to a dried powder. The tubers were minced in a chopper and the tissues dried in enamelled trays without allowing them to ferment. The material was ground to a fine powder and sieved through a fine mesh and preserved in closed bottles. The enzyme was extracted in 20% alcohol solution and tested.

Procedure.—Linter's soluble starch was used as a substrate in all experiments. The hydrogen ion concentration of the mixtures was adjusted by Walpole's acetate buffers between p_H range 3·0-6·5 and Sörensen's phosphate buffers for higher ranges. The enzyme solutions were obtained by suitably diluting the extracts obtained from different stages of purification. Activity was measured by obtaining the CuO precipitated by the converted invert sugars with Fehling's solution as recommended by Sherman, Kendall and Clark (*J. Amer. Chem. Soc.*, 1910, **32**, 1073). The dry matter in the solution of the enzyme used in the reaction was determined in each case by drying an aliquot portion of the extracts at 105° to a constant weight. The reactions were carried out at constant temperature in an electrically controlled thermostat. The digestions were carried out in Erlenmeyer flasks with 100 c.c. of a 2% soluble Linter starch solution, enzyme solutions, and buffers.

Detection of Amylase in the dried Powders.—The powder (50 g.) in each case was extracted with 500 g. of pure distilled water, buffered at p_H 5·4, triturating in a mortar and occasionally shaking at 37° for 24 hours. To avoid contamination and to facilitate extraction 20% redistilled alcohol was mixed with water. The extracts, thus obtained, were allowed to settle in the cold at 4°, decanted, filtered and used in the experiment.

As the extracts contained soluble sugars a blank was also taken in each case to allow for the glucose due to extract and starch which was subtracted from the total weight of CuO obtained to get the reaction due to the enzyme action.

TABLE II

Starch solution (2%) = 100 c.c. Buffer (p_H = 5·4), 10 c.c. Enzyme solution = 4 c.c.
Temp. of reaction = 36·5° ± 0·1°. Time of reaction = 1 hr.

Extract taken.	Total solids in the extract.	CuO blank.	CuO due to extract.	CuO due to enzyme.
Sweet potato	0·2512 g.	0·4482 g.	1·2563 g	0·8081 g.
Arvi	0·5442	0·2800	0·8243	0·5443
Banda	0·4604	0·2365	0·6969	0·4614
Zimikand	0·1430	0·2012	0·2581	0·0469

The presence of amylase was indicated in each of the above materials and sweet potato was found to be the richest amongst them. The activity of the amylase from Zimikand was found to be the least both in case of its pressed juice as well as the powdered starch indicating that it is not a rich source of enzyme.

Purification of the Enzyme.—The most authentic method employed for the purification was that employed by Sherman, Caldwell and Doebbeling (*J. Biol. Chem.*, 1934, **104**, 501). Their method was to fractionate the extracts of barley-malt with ammonium sulphate followed by dialysis and repeated fractional precipitation with alcohol.

Dialysis.—A preliminary dialysis was employed using collodion membrane to get rid of the adhering sugars and salts from the extract at 15°.

TABLE III

Period of dialysis.	Zimikand: Total solids in 5 c.c.	Zimikand: CuO due to enzyme.	Sweet potato: Total solids in 5 c.c.	Sweet potato: Cuo due to enzyme.	Arvi: Total solids in 5 c c.	Arvi: CuO due to enzyme.	Banda: Total solids in 5 c.c.	Banda: Cuo due to enzyme.
Original extract	0·4532 g.	0·5600 g.	0·2512 g	0·8081 g.	0·5142 g.	0·6064 g.	0·4132 g.	0·9300 g.
2 hours	0·2351	0·4513	0·1463	0·7512	0·3241	0·5014	0·3151	0·7200
4 ,,	0·1932	0·4615	0·0873	0·7613	0 2140	0·5132	0·2512	0·7100
5 ,,	0·1083	0·4732	0·0788	0·7422	0·2013	0.5200	0·1460	0 6900
6 ,,	0·096	0·4700	0 0780	0·9754	0·1465	0·5215	0·090	0 6800
8 ,,	0·097	0·4530	0·0780	0·9700	0·1460	0·5000	0·091	0 6573

It was found that after six hours' dialysis the purification was effected and further dialysis caused loss of the enzymic activity. So for next batches six hours' dialysis was employed.

Precipitation with Ammonium Sulphate and Alcohol.—On the basis of the findings in the previous paper by the author (*J. Indian Chem. Soc.*, 1942, **19**, 121) 400 c.c. of the dialysed extract were taken and 160 g. of pure ammonium sulphate added. The solution was well stirred and left in the frigidaire for 70 hours. The supernatant liquid was filtered off by upward microfiltration and solids washed with alcohol and ether. The solids were then dissolved in distilled water, buffered at p_H 5·6 using Walpole's acetate buffer and dialysed free from sulphate. The enzyme preparations were then further purified by precipitation with alcohol.

The dialysed solution in each case was mixed with enough absolute alcohol to obtain a strength of 50% by volume and any precipitate obtained removed by upward filtration. The strength of the solution was then further raised to 75% alcohol. The precipitates thrown out were separated and dissolved in double distilled water. A portion dissolved in double distilled water was used for determination of optimum p_H. The activity of the purified enzyme preparations is given in Table IV.

TABLE IV

Enzyme = 2 c.c. Starch (2% soln.) = 80 c.c. Buffer = 20 c.c. Time of reaction = 1 hour.
Temp. = 37° ± 0·1°.

Source of enzyme.	Dry weight of enzyme.	CuO due to enzyme
Sweet potato	0·0071 g	0·8941
Arvi	0·0281	0·2475
Banda	0·0324	0·2782
Zimikand	0·0301	0·1789
Malt	0·0628	0·2883

TABLE V

Starch (2% soln.) = 80 c.c. Buffer = 20 c.c. Time of reaction = 1 hour.
Temp. = 37° ± 0·1°.

Source of enzyme	Optimum temperature	Optimum p_H
Sweet potato	50-55°	5·0-5·2
Banda	55°	5·6-6·0
Arvi	55-60°	6·0
Malt extract	55°	5·0-5·2

The optimum of Zimikand could not be determined due to the purified preparation being lost and fresh tubers being not available till the next season.

From the study on the optimum p_H it can be seen that the optimum p_H of sweet potato (white variety) resembles malt amylase as reported by Giri (*J. Indian Chem. Soc.*, 1934, **11**, 339) and is saccharogen amylase (β-amylase). But the p_H of Arvi and Banda have their optimum between 5·6-6·0. Their optimum p_H resembles more the α-amylases occurring in *Aspergillus Oryzae* which as reported by Caldwell and Tyler (*J. Amer Chem. Soc.*, 1931, **53**, 2316) lies at p_H 5·3 to 5·5 at 40° with 0·01*M*-acetate buffer. The optimum temperature is 55° in all cases.

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CHARGE AND STABILITY OF COLLOIDS. PART VII. KINETICS OF COAGULATION OF As_2S_3 SOL WITH AND WITHOUT ADDITION OF NON-ELECTROLYTE

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The influence of non-electrolytes as studied against electrolyte coagulation has often given conflicting results even with the same sol and the same non-electrolyte. Attempts have been made to find out the influence of non-electrolytes such as methyl alcohol, ethyl alcohol, sugar, gelatine and agar-agar by following the kinetics of coagulation according to Smoluchowski's equation. The results reveal that methyl alcohol accelerates, whereas other non-electrolytes retard the process. This confirms the previous view that methyl alcohol sensitises the sol while other non-electrolytes protect it.

In previous communications (*J. Indian Chem. Soc.*, 1943, **20**, 25, 110) the effect of non-electrolytes on the adsorption of oppositely charged ions has been studied. It has been shown that in presence of methyl alcohol, the adsorption of oppositely charged ions decreases, whereas with ethyl alcohol, agar-agar, glucose, sucrose and gelatine, an increase in the adsorption takes place. Methyl alcohol is also known to sensitise whereas other non-electrolytes stabilise the colloid. Sensitisation or stabilisation is usually measured in terms of the quantity of electrolyte necessary to coagulate a particular quantity of the sol. Another method employed to measure sensitisation or stabilisation is to measure cataphoretic velocity of a particle of a colloid with a particular electrolyte. Mukherjee and co-workers (*Trans. Nat. Inst. Sci. India,* 1935, **1**, 47) observed a decrease in cataphoretic velocity when sugar was added, whereas he had observed an increase in the 'chemical adsorption' (*loc. cit.*). Patel and Desai (*Kolloid Z.*, 1930, **51**, 318) have observed a sensitising influence of sugar on thorium hydroxide sol which they subjected to progressive dialysis, whereas Mata Prasad and Nabar (*J. Indian Chem. Soc.*, 1932, **9**, 609) observed a stablising effect of sucrose and glucose on ceric hydroxide sol. Ghosh and Dhar (*J. Phys. Chem.*, 1925, **29**, 668) obtained a sensitising effect of sugar on As_2S_3 sol.

The various observers thus appear to have obtained contradictory results with the same colloid (As_2S_3 sol) and the same non-electrolyte (sugar).

To us it appears that measurement of coagulation velocity of carefully purified sols in presence of pure non-electrolytes may give results which will be of use in arriving at a conclusion regarding this phenomenon.

In this paper attempts have been made to find out, if any effect is produced on the rate of coagulation of a colloid in presence of various non-electrolytes. A method similar to Paine (*Koll.-Chem. Beih.*, 1912, **4**, 24) has been followed.

Experimental

As_2S_3 sol was prepared as in previous communications of this series (*loc. cit.*). The sol (5 c.c.) was taken in several bottles and the sol-electrolyte was made up to 10 c.c. in each case. Each bottle was shaken after the addition of electrolyte so as to have a homogeneous mixture and the contents filtered after 5 minutes' interval successively and the quantity of As_2S_3 left was measured by Kessler's method. In the beginning, coagulating concentration of $BaCl_2$ was determined that could coagulate As_2S_3 sol without addition of any non-electrolyte in an hour. The same concentration was used throughout irrespective of the fact that the non-electrolytes added protected or sensitised the sol. Increasing concentrations of methyl alcohol, ethyl alcohol, sugar, agar-agar and gelatine were added to the sol and the changes in the rate of coagulation of As_2S_3 sol were determined.

The coagulation velocity constant was determined by using the formula,

$$\gamma_1=\frac{\gamma_0}{(1+\beta t)^2} \text{ or } \beta=\frac{1}{t}\left(\sqrt{\frac{a}{a-x}}-1\right)$$

and k, the bimolecular constant was also determined from the equation,

$$k=\frac{1}{t}\cdot\frac{x}{a-x}.$$

To avoid complications arising out of the formation of agglomerates all observations were taken for the first thirty minutes when no visible particles were formed. We have taken the particles of original sol to be proportional to γ_0 and the concentration after a time t denoted by $a-x$, to be proportional to γ_1. Here the uncoagulated sol is taken to consist of primary particles which are proportional to γ_1 and consequently equation $\gamma_1=\frac{\gamma_0}{(1+\beta t)^2}$ has been used (*cf.* Joshi, *J. Indian Chem. Soc.*, 1931, **8**, 11). As the process followed here is the same in all the experiments, so even if there is any doubt about the concentration representing the number of particles, it is almost certain that the method gives a fair idea of the relative changes that are taking place in the sol.

The results obtained are given in the following tables and shown graphically in Fig. 1.

TABLE I

Conc. of As_2S_3 sol = 3·69 g./litre. 5 C.c. of sol + 1 c.c. of 0·01 N-$BaCl_2$ + 4 c.c. of distilled water.

Time.	$a-x$.	$\beta \times 10^3$.	$k \times 10^3$.
0 min.	0·01845 g.	0·00	0·00
5	0·01537	19·12	40·07
10	0·01230	22·50	50·00
15	0·01050	21·70	50·50
20	0·00855	23·43	57·90
25	0·00740	23·16	59·70
30	0·00630	23·75	64·30

In the following tables the column $a-x$ has been omitted in order to condense the tables

TABLE II

5 C.c. sol + increasing conc. of MeOH + 1 c.c. of 0·01 N-$BaCl_2$ + water.
Total vol. = 10 c.c.

Time.	Volume of methyl alcohol							
	1 c.c.		2 c.c.		3 c.c.		4 c.c.	
	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.
5 min.	26·40	56·25	30·00	64·50	36·40	79·50	49·0	100·0
10	25·60	57·70	31·30	72 44	37·20	88·27	41·63	100·5
15	26·50	63·50	31 24	77·18	35·87	91·05	48·80	133·3
20	24·10	59·80	28·45	73·02	37·68	103·80	48·02	142·2
25	25·41	67·00	32·00	89·50	40·98	124·03	50 56	165·0
30	26·63	74·55	32·02	94·80	41·10	132·9	47·98	165·2

TABLE III

5 C.c. of As_2S_3 sol + increasing quantity of EtOH + 1 c.c. of 0·01N-$BaCl_2$ + the requisite amount of water to make total volume 10 c.c.

Volume of ethyl alcohol

Time.	1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$.	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 14^3$.	4 c.c. $k \times 10^3$.
5 min.	16·10	33·54	14·10	29·20	9·80	15·80	11·80	24·30
10	16·60	36·67	12·05	25·50	9·80	20·60	14·40	30·85
15	17·05	38·46	12·77	27·95	9·60	20·60	13·38	29·43
20	20·45	49·20	12·79	28·80	11·25	25·05	14·75	33·87
25	18·74	46·30	14·61	34·60	11·56	26·50	14·60	34·56
30	18·61	47·60	15·20	37·60	12·18	28·80	13·63	32·80

TABLE IV

5 C.c. of As_2S_3 sol + increasing quantity of sugar + 1 c.c. of 0·01 N-$BaCl_2$ + the requisite volume of water to make the total volume 10 c.c.

Volume of 10% solution of sugar

Time	1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 10^3$.	4 c.c. $k \times 10^3$.
5 min.	15·40	32 08	7 20	14·53	6·00	12·07	4·20	8·50
10	15·60	33 70	14·40	30·85	7·22	14·95	3·90	7·90
15	17.05	38·46	11·30	24·45	6·53	13 70	3·20	6·55
20	15·36	35·40	9·79	21·50	7·20	15·43	3·61	7·50
25	16 36	39·40	9·00	20·05	7·80	17·20	4·22	8·90
30	16·07	39·87	9·67	22·08	8·53	19·23	3·65	7·70

TABLE V

5 C.c. of As_2S_3 sol + increasing quantity of gelatine (0·25%) + 0·01N-$BaCl_2$ + the requisite volume of water to make up the total volume 10 c.c.

Volume of gelatine (0·25%)

Time.	1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$.	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 10^3$.	4 c.c. $k \times 10^3$.
5 min.	11 50	23·63	7·80	15·80	6·00	11·73	4·20	8·47
10	12·05	25·51	7·70	15 04	5·75	11·81	3·90	7·89
15	9·60	20·56	5·83	12·18	4·92	10·45	3·00	6·11
20	7·84	16·85	4·65	9 71	3·85	8·02	2·70	5·57
25	6·76	14·67	4·38	9·20	3·50	7·31	2·36	4·86
30	6·67	13·26	4·02	8·50	3·10	6·47	2·13	4·40

TABLE VI

5 C.c. of As_2S_3 sol + increasing quantity of agar-agar (0·24%) + 0·01N-$BaCl_2$ + the requisite volume of water to make up the total volume 10 c.c.

Time.	Volume of agar-agar (0·25 %)							
	1 c.c.		2 c.c.		3 c.c.		4 c.c.	
	$\beta \times 10^3$	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.
5 min.	14·10	29·20	11·50	23·63	9·60	19·64	8·68	17·70
10	14·40	30·85	9·80	20.58	8·75	18·27	7·70	16·04
15	11·30	24·44	9·30	19·95	8·03	17·01	6·53	13·73
20	9·79	24·14	8·13	17·58	7·01	16·38	5·45	11·50
25	8·40	18·57	7·28	15·91	6·24	13·48	5·27	11·25
30	7·50	16·67	6·53	14·34	5·63	12·22	4·80	10·29

DISCUSSION

From the results recorded above and shown graphically in Fig. 1, it is clear that β remains almost constant when no non-electrolyte is added. With non-electrolytes β either slightly increases (as with MeOH and sugar), or decreases (as with gelatine and agar-agar.)

In the case of methyl alcohol the β values for the same time interval increases when the concentrations of the non-electrolyte increase, whereas with other non-electrolytes β values decrease. Increase of β values with increase of methyl alcohol concentration signifies that the velocity of coagulation increases. This may be intimately connected with sensitisation, because if the stability of the colloid decreases, the velocity of coagulation will increase. In the case of other non-electrolytes *e.g.* ethyl alcohol, sugar, gelatine and agar-agar the β values decrease with increasing quantities of the non-electrolyte. This means the increase of the non-electrolytes produces more stability.

In this connection it may be noted that hitherto the action of non-electrolyte on any colloid as measured against electrolyte coagulation gave divergent results even with the same colloid and the same non-electrolyte.

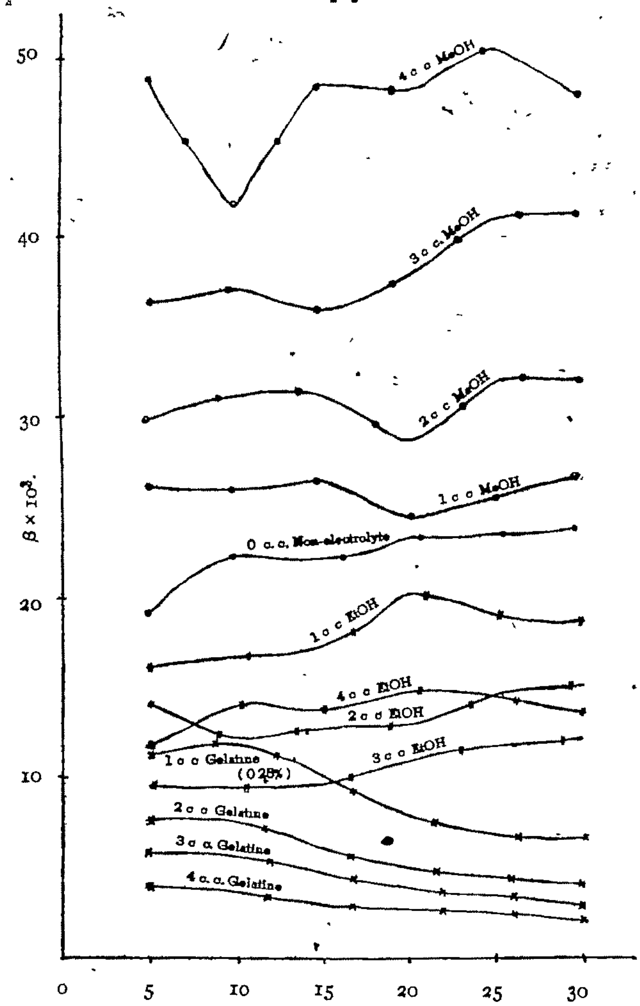
Present observations on the effect of a non-electrolyte on a colloid by study of the coagulation velocity by Paine's method reveals a consistent result in so far as methyl alcohol accelerates the rate of coagulation. This acceleration is in conformity with the increase in the adsorption of oppositely charged ions by As_2S_3 sol in presence of methyl alcohol. Both these facts explain the sensitisation observed with methyl alcohol and arsenious sulphide sol. With other non-electrolytes *e.g.* ethyl alcohol, sugar, agar-agar and gelatine we find that the velocity of coagulation decreases indicating a slowing down of the coagulation process, which is in conformity with the protection observed with these non-electrolytes.

It is interesting to note that the value of β shows a slight tendency to increase with methyl alcohol, ethyl alcohol and sugar in the case of arsenious sulphide sol, whereas with agar-agar and gelatine it shows a distinct tendency to decrease. If in conformity with previous workers a constancy or even a slight tendency to increase in β values is taken as a characteristic property of rapid coagulation, we have to assume that arsenious sulphide sol with the addition of the non-electrolytes *e.g.*, methyl alcohol, ethyl alcohol and sugar, maintains the character of rapid coagulation, while when gelatine and agar-agar are added to the same arsenious sulphide sol, the value of β decreases indicating that the coagulation has a tendency to become slow. Thus we see that the character of coagulation of the same sol changes gradually on the

addition of non-electrolytes. There cannot be any appreciable change in the electric charge of a colloid on adding a non-electrolyte, but the effective collisions between the particles may con

FIG. 1

As_2S_3 sol.



Time in min.

siderably decrease and thus reduce the value of ϵ, the probability factor. This suggests that ϵ may be made to change by suitably changing the concentration of the non-electrolyte in question, while the charge remains the same.

There are some discontinuities in β-time curve with MeOH and As_2S_3, whereas such discontinutes are not observable with $Fe(OH)_3$ sol (*J. Indian Chem. Soc.*, 1944, **232**). This may be in some way connected with the nature of the As_2S_3 sol.

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CHARGE AND STABILITY OF COLLOIDS. PART VIII. KINETICS OF COAGULATION OF $Fe(OH)_3$ SOL WITH AND WITHOUT ADDITION OF NON-ELECTROLYTE

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The effect of methyl alcohol, ethyl alcohol, sugar, agar-agar and gelatine has been studied with $Fe(OH)_3$ sol. In the case of methyl alcohol the β values increase with increasing quantities, showing sensitisation and with other non-electrolytes decrease indicating protection. It has been found that βt remains constant, where t is the time required to reach a fixed stage of coagulation with increasing quantities of any non-electrolyte. A distinction between slow and rapid coagulation has been drawn on this.

In a previous paper (*J. Indian Chem. Soc.*, 1944, **21**, 227) it has been shown that methyl alcohol accelerates whereas ethyl alcohol, sugar, gelatine and agar-agar retard the coagulation velocity of As_2S_3 sol. In this paper the influence of the above non-electrolytes has been studied with ferric hydroxide sol.

Experimental

Ferric hydroxide sol was prepared by the method given in a previous communication of this series (*J. Indian Chem. Soc.*, 1943, **20**, 25). The method of procedure for the determination of the coagulation velocity was exactly the same as given in the previous paper. The results obtained are given below and plotted in Fig. 1.

Conc. of $Fe(OH)_3$ sol = 12 g./litre (as Fe_2O_3). Chlorine content of the sol = 0·016 g./litre Hence purity of the sol (Fe_2O_3/Cl) = 750.

Table I

5 C.c. of $Fe(OH)_3$ sol + 1 c.c. of 0·07N-K_2SO_4 + 4 c.c. of water.

Time.	$a-x$.	$\beta\times10^3$.	$k\times10^3$.
0 min.	0·060	0·00	0·00
5	0·051	16·90	35·29
10	0·044	16·80	36·36
15	0·040	15·00	33·33
20	0·037	13·70	31·08
25	0·034	13·14	30·59
30	0·032	12·32	29·18

In the following tables the column $a-x$, has been deleted to conserve space in order to condense the tables.

Table II

5 C.c. of $Fe(OH)_3$ sol + increasing quantity of methyl alcohol + 1 c.c. of 0·07 N-K_2SO_4 + requisite volume of water to make up to 10 c.c.

Methyl alcohol

Time.	1 c.c		2 c.c.		3 c.c.		4 c.c.	
	$\beta\times10^3$.	$k\times10^3$.	$\beta\times10^3$.	$k\times10^3$.	$\beta\times10^3$.	$k\times10^3$.	$\beta\times10^3$.	$k\times10^3$.
5 min.	200·0	599·9	229·8	723·2	278·1	942·7	349·8	1300
10	133·55	445·40	173·9	650·0	192·8	757·2	230·3	990·9
15	105·50	377·9	128·5	504·8	144·13	599·9	231·5	1267
20	82·90	303·0	101·95	411·7	123·20	550·0	195·0	1150
25	69·56	260·0	86·50	360·0	115·12	560·0	179·12	1160
30	64·30	252·4	76·8	330·3	104·70	538·0	149·3	996·5

TABLE III

5 C.c. of $Fe(OH)_3$ sol + increasing quantity of ethyl alcohol + 1 c.c. of 0·07 N-K_2SO_4 + requisite volume of water to make up to 10 c.c.

Time.	Ethyl alcohol 1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$.	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 10^3$.	4 c.c. $k \times 10^3$.
5 min.	146·5	400·0	130·3	345·5	109·9	280·1	87·7	213·8
10	114·9	361·6	100·0	300·0	87·9	253·0	73·25	200·0
15	89·3	297·0	76·6	241·0	66·6	200·0	58·6	168·6
20	72·50	250·0	66·8	222·7	53·5	164·3	46·8	137·5
25	63·30	226·7	58·0	200·0	46·0	144·6	38·7	114·9
30	57·96	216·6	52·75	188·9	41·20	133·3	33·3	100·0

TABLE IV

5 C.c. of $Fe(OH)_3$ sol + increasing quantity of sugar (10%) + 1 c.c. of 0·07 N-K_2SO_4 + requisite volume of water to make up to 10 c.c.

Time.	Sugar solution (10%) 1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$.	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 10^3$.	4 c.c. $k \times 10^3$.
5 min.	200·0	600·0	155·4	432·1	130·3	345·5	116·2	300·0
10	158·25	566·8	123·6	400·0	100·0	300·0	82·6	233·4
15	128·5	504·8	105·5	377·9	82·4	266·7	66·7	200·0
20	108·1	450·0	84·4	303·0	66·8	222·7	57·5	180·8
25	98·6	440·0	69·6	260·0	58·0	200·0	49·4	160·0
30	82·1	366·7	64·3	252·4	52·75	188·9	44·5	148·5

TABLE V

5 C.c. of $Fe(OH)_3$ sol + increasing quantity of gelatine (0·25%) + 1 c.c. of 0·07 N-K_2SO_4 + requisite volume of water to make up to 10 c.c.

Time.	Gelatine solution (0·25%) 1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$.	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 10^3$.	4 c.c. $k \times 10^3$.
5 min	78·30	187·10	65·72	152·95	58·20	133·3	58·20	133·30
10	43·86	106·90	41·75	100·00	32·86	76·47	30·90	71·42
15	34·62	87·19	32·70	81·48	26·10	62·36	23·24	54·55
20	30·80	80·44	27·45	70·02	21·90	53·46	20·72	50·00
25	26·05	69·10	24·62	64·36	20·80	52·31	19·60	48·89
30	23·01	61·92	21·72	57·58	18·30	50·00	18·32	46·68

TABLE VI

5 C.c. of $Fe(OH)_3$ sol + increasing quantity of agar-agar (0·25%) + 1 c.c. of 0·07 N-K_2SO_4 + requisite volume of water to make up to 10 c.c.

Time.	Agar-agar (0·25%) 1 c.c. $\beta \times 10^3$.	1 c.c. $k \times 10^3$.	2 c.c. $\beta \times 10^3$.	2 c.c. $k \times 10^3$.	3 c.c. $\beta \times 10^3$.	3 c.c. $k \times 10^3$.	4 c.c. $\beta \times 10^3$.	4 c.c. $k \times 10^3$.
5 min.	58·20	133·80	51·30	115·8	48·10	107·65	39·04	85·72
10	37·00	87·53	32·86	76·47	29·10	66·66	25·66	57·89
15	29·24	71·27	26·10	62·36	23·24	54·55	20·60	47·61
20	27·59	70·02	23·18	57·14	21·90	43·76	19·66	46·78
25	24·62	64·36	20·80	52·31	18·54	45·71	17·50	42·77
30	23·00	61·92	18·32	46·68	17·30	43·39	16·30	40·74

DISCUSSION

With $Fe(OH)_3$ sol the β values show a distinct tendency to fall with time in the case of all the non-electrolytes for any concentration of these non-electrolytes, but all these curves are alike. Here also we find with methyl alcohol that β increases for the same time interval whereas with other non-electrolytes it decreases with increasing quantities of the non-electrolytes added.

The values of $a-x$, the uncoagulated mass can also be plotted with increase in time and it can be observed that in the case of $Fe(OH)_3$ sol. these curves become steeper with non-electrolytes than the one without non-electrolytes, including methyl alcohol, but with the latter the curves are different from the rest in so far that methyl alcohol increases the steepness of the curve with increase in the concentration whereas with other non-electrolytes the slope of the curves decreases as their concentration increases. From this it appears that methyl alcohol produces a different effect than other non-electrolytes, which is to be expected from its sensitisation effect.

From the values given in the above tables, $(a-x)-t$ and $\beta-t$ curves have been obtained. From these figures we can find out the time required to produce a definite stage of coalescence, *e.g.*, we find t values for a fixed value of $(a-x)$. After knowing these t values we can read from $\beta-t$ curves the corresponding β values. From the values so found graphically, the product βt has been calculated and recorded in the following table.

FIG. 1

F(OH)₃ sol.

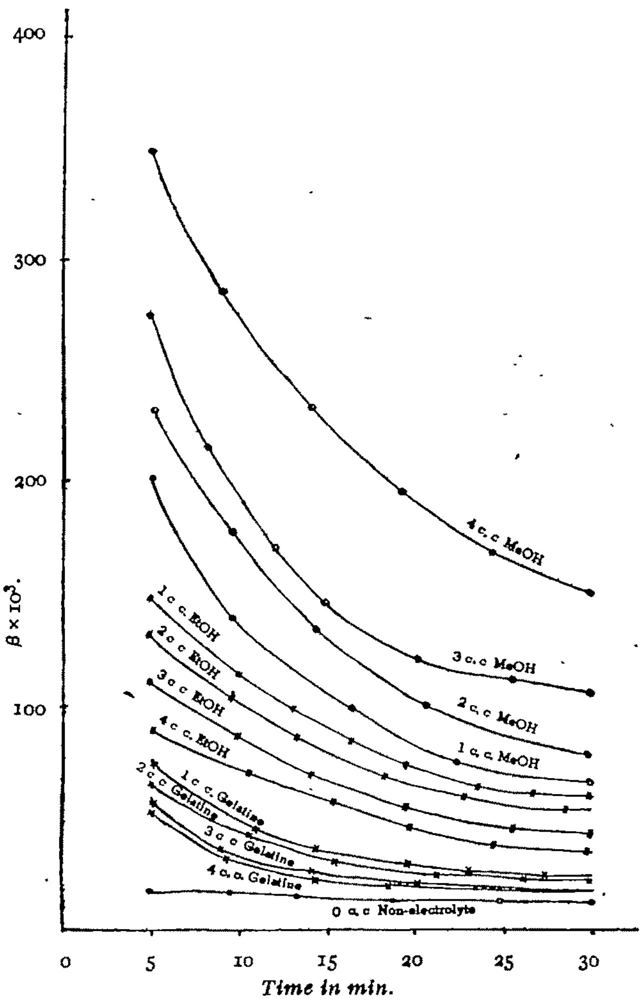

TABLE VII

βt values with varying quantities of non-electrolytes.

Quantities of the non-electrolyte	As_2S_3 sol. 1 c.c.	2 c.c.	3 c.c.	4 c.c.	$(a-x)\times 10^3$.	$Fe(OH)_3$ sol. 1 c.c.	2 c.c.	3 c.c.	4 c.c.	$(a-x)\times 10^2$.
Methyl alcohol	416·0	439·6	425·5	420·0	9	1334	1523	1474	1440	1 0
Ethyl alcohol	238·0	214 2	241·5	252·0	12	1045	1000	986	999	1 5
Sugar (10%)	116·2	142·5	104·0	120·0	15	1000	1043	1000	952	1·5
Gelatine (0·25%)	57·5	58·5	58·0	56·2	16·5	455	415	416	451	3·0
Agar-agar (0 25%)	157·5	99·75	128·0	128·0	15·0	412·5	412·5	409·5	416·3	3·0

The above values of βt calculated from the $(a-x)$ values are not for the same stage of coagulation with all the non-electrolytes.

The stage of coagulation has to be different with different non-electrolytes depending on the nature of the curves, but with each non-electrolyte there is a fixed stage of coagulation.

From Table VII we see that the product βt remains almost constant, though the β values go on changing with time in the case of $Fe(OH)_3$ sol. From the equation

$$r_1 = \frac{r_0}{(1+\beta t)^2} \quad \text{or} \quad \beta = \frac{1}{t}\left(\sqrt{\frac{r_0}{r_1}} - 1\right)$$

it is clear that in order to make β values constant for various values of t we must have the relation between $r_1' : r_1'' : r_1''' : r_1''''$ etc., the number of primaries after the time t_1, t_2, t_3, t_4 etc., as follows:

$$r_1' : r_1'' : r_1''' : r_1'''' :: \frac{1}{(1+\beta t_1)^2} : \frac{1}{(1+\beta t_2)^2} : \frac{1}{(1+\beta t_3)^2} : \frac{1}{(1+\beta t_4)^2}$$

The above ratios give us the decrease in the values of r_1, when the times are varying, but β does not remain constant in slow coagulation and hence the decrease in r_1 is slower than that indicated by the above relation.

On the other hand, when r_1 is given a fixed value in the equation

$$r_1 = \frac{r_0}{(1+\beta t)^2}.$$

We can see that βt should remain constant, irrespective of the variation in t. Therefore if we can find out the time necessary to produce a fixed stage of coagulation *i.e.*, the time required to reach a fixed value of r_1, we should find that βt is constant. This is exactly what is found from the above experiments. Therefore we are justified in saying that the kinetics of coagulation in the above experiments have proceeded in accordance with Smoluchowski's theory.

Smoluchowski suggested that the equation

$$r_1 = \frac{r_1}{(1+\beta t)^2} \quad \text{should be} \quad r_1 = \frac{r_0}{(1+\epsilon\beta t)^2} \quad \text{for slow coagulation}$$

we can put $\epsilon\beta = B$, where B is the β value for slow coagulation.

We have seen that B changes with time but the time required to bring about a definite stage of coalescence is proportional to B values *i.e.* t varies inversely as B.

Therefore, $\quad t_1 B_1 = t_2 B_2 = t_3 B_3 = t_4 B_4$ etc.,

or $\quad t_1 \epsilon_1 B = t_2 \epsilon_2 B = t_3 \epsilon_3 B = t_4 \epsilon_4 B$ etc., where B is the velocity of coagulation when no non-electrolyte is added,

or $\quad t_1 \epsilon_1 = t_2 \epsilon_2 = t_3 \epsilon_3 = t_4 \epsilon_4$ etc.,

or $\quad t_1 : t_2 : t_3 : t_4 :: \frac{1}{\epsilon_1} : \frac{1}{\epsilon_2} : \frac{1}{\epsilon_3} : \frac{1}{\epsilon_4}$ etc.

This means that the reciprocal of the time required to produce a definite stage of coalescence is proportionl to ϵ, the probability factor. We know that probability factor varies, and from the above it is clear that ϵ varies inversely as the time required to bring about the same stage of coagulation. Therefore we can say that the difference between the rapid and the slow coagulation is this that in rapid coagulation the β values remain constant and further βt is also constant for the same stage of coagulation, it means that the time required to bring about the same stage of coagulation will be the same when various electrolytes are added. In slow coagulation region as β decreases, and further here also βt remains constant, the time required to reach the same stage of coagulation will proportionately increase, so that Smoluchowski's theory gives that in the slow coagulation region β must decrease but the decrease in β must be proportional to the increase in t, the time required to reach the same stage of coagulation in a set of experiments, whereas in the region of rapid coagulation both β and the time required to produce the same stage of coagulation remain constant (*cf.* Mukherjee and Papaconstantinou, *J. Chem. Soc.*, 1920, **117**, 1563).

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PHOTOIODINATION OF SODIUM TARTRATE IN AQUEOUS SOLUTION

By J. L. MUKHERJEE AND P. C. GOSWAMI

Sodium tartrate was iodinated with aqueous iodine in presence of light of different wave-lengths, at different temperatures and different concentrations of acceptor and active molecules

Most of the photoiodinations, that have been investigated, were done in presence of KI. Iodine is not much soluble in water and hence a concentrated solution of I_2 cannot be obtained. In aqueous solution in presence of KI, however an additional complexity is brought into the reaction, for in presence of KI an additional reaction $KI+I_2=KI_3$ occurs.

In reaction in aqueous solution, this complexity can be avoided and it may be expected that in aqueous solution iodination may be also similar to other photohalogenation processes such as brominations.

Dhar (*Proc. K. Akad. Wetensch, Amsterdam*, 1916, **18**, 1097) first showed that sodium tartrate can be iodinated in presence of light. Dhar and Bhattacharyya studied the reaction in presence of KI and found that the reaction is unimolecular (*J. Indian Chem. Soc.*, 1929, **6**, 147). They studied the reaction under different wave-lengths of light and at temperature 20°, 30° and 40°. Photoiodination of sodium tartrate in aqueous solution has not been studied till now although photoiodination of some other salts such as potassium oxalate (Dhar, Bhattacharyya and Mukherjee, *J. Indian Chem. Soc.*, 1935, **12**, 151), sodium formate (Bhagwat, *ibid.*, 1940, **17** 304) in aqueous solution has been investigated. With the end in view mentioned above we investigated the reaction and found certain peculiarities as noted below.

EXPERIMENTAL

Resublimed I_2 was mixed with one-fourth its weight of KI and sublimed again. This I_2 was dissolved in conductivity water by shaking in a shaker. Sodium tartrate (E. P. Merck) was recrystallised from conductivity water and dissolved in conductivity water. The solutions of I_2 and sodium tartrate were kept in a thermostat and mixed in the dark. Immediately 3 c.c. of the mixture were withdrawn and titrated with approximately 0·001*N* $Na_2S_2O_3$ by using a microburette. The source of light was a point-o-lite lamp of 100 C. P. By keeping the centre of the lamp at a distance of 27·5 cm. from the reaction cell, the intensity of light was kept the same throughout the experiment. The mixture in the reaction cell was then exposed to light kept parallel by means of a lens. Heat rays were cut off by allowing the light to pass through a filter of *N*/20 $CuSO_4$ solution. At various intervals of time, measured by means of a stop-watch, 3 c.c. of the reaction mixture were withdrawn and titrated mith approximately 0·001*N*-$Na_2S_2O_3$ using a microbruette. By means of Wratten filters, lights of different wave-lengths were separated.

Since for every withdrawal of 3 c.c. of the reaction mixture, a vacuous space occurred into which I_2 could vaporise and since I_2 might also diffuse through the reaction cell, it was hence first investigated whether any error occurred due to these two factors. The escape of I_2 due to these factors was found quite negligible.

Table I gives the reaction rate in dark at 20°. The dark reaction is unimolecular. k is the unimolecular constant catculated from $k=\frac{1}{t}\log\frac{a}{a-x}$.

TABLE I

Sodium tartrate ($0·42N$) + I_2 (aq.) ($0·1614\ N/100$). Temp = 20°

Time.	$Na_2S_2O_3$.	k.	Time.	$Na_2S_2O_3$.	k.
0 min.	5·15 c.c.	—	120	4·91	0·0001725
60	5·03	0·00017	180	4·79	0·000175
			—	Mean k	0·0001725

Concentrations in brackets always represent the final concentrations after mixing the reactants.

Table II gives the reaction rate when exposed to lights of different wave-lengths. In presence of light, it has been noticed that the unimolecular constant k progressively decreases. There is, due to some cause as yet unknown, a rapid consumption of I_2 at the beginning. This large consumption of I_2 at the beginning is responsible for the diminution of unimolecular constant, for it is superimposed upon the reaction which is afterwards strictly unimolecular. Hence the unimolecular constant should be calculated not from zero time but by eliminating the first reaction. When this is done it is found that k again becomes constant. k' is the unimolecular constant calculated by eliminating the first reading. It may be pointed out here that in photobromination of tartaric acid by Ghosh and Basu (*J. Indian Chem. Soc.*, 1925, **2** 163; 1928, **5**, 342) there was observed also a progressive diminution of unimolecular constant k. To explain this they evaluated an equation (*ibid.*, 1928, **5**, 361) and obtained a constant by its application. In the present case a uniform value of the constant has always been obtained when k was calculated from the second reading of titration.

TABLE II

Time = 20°, Na-tartrate ($0·42N$) + I_2, aq. ($0·1614 \times 10^{-2}N$).

White light.				Blue light (408·5-490·5 $\mu\mu$)		
Time.	$Na_2S_2O_3$.	k.	k'.	$Na_2S_2O_3$.	k.	k'.
0 min.	5·17 c.c.			5·21 c.c.		
10	4·74	0·00377		4·82	0·00338	
30	4·56	0·00182	0·00084	4·67	0·00158	0·000685
60	4·30	0·00133	0·000846	4·45	0·00114	0·00069
120	3·83	0·00108	0·00084	4·05	0·00091	0·000686
180	3·44	0·000982	0·00082	3·65	0·00086	0·00071
		Mean k'	0·000836		Mean k'	0·000692

Greenish blue light (442—489·5 $\mu\mu$)				Red light (645 to 595 $\mu\mu$)		
Time.	$Na_2S_2O_3$	k.	k'.	$Na_2S_2O_3$.	k.	k'
0 min.	5·56 c.c.			5·59 c.c.		
10	5·30	0·00208		5·44	0·00118	
30	5·18	0·00103	0·00050	5·17	0·00113	
60	5·0	0·00077	0·000506	5·02	0·00078	0·00042
120	4·66	0·00064	0·000508	4·75	0·00059	0·000408
180	4·37	0·00058	0·000492	4·46	0·00054	0·000428
		Mean k'	0·000501		Mean k'	0·000418

It appears from Table II that the reaction rate is greatest in presence of white light and decreases as the wave-length is increased. The dark reaction is negligibly small in comparison with light reactions.

Table III summarises the reaction rate at different concentrations of sodium tartrate at a constant concentration of I_2 and Table IV, the same at different concentrations of I_2 but at a constant concentration of sodium tartrate. All the reactions are studied in presence of white light and at temperature 20°. Since in all these cases, also, there is a progressive diminution of k the unimolecular constant calculated from zero time, as noticed in the data supplied for different wavelengths, the values of k' only, which for each of these experiments had always a good constant value, have been given and compared.

TABLE III

Constant conc. of $I_2 = 0{\cdot}1614 \times 10^{-2}\ N$.

Conc. of Na-tartrate	k'.
0·21 N	0·000561
0·42	0·000836
0·84	0·00115
1·26	0·00152

TABLE IV

Constant conc. of Na-tartrate=0.042 N.

Conc. of Na-tartrate.	k'.
0·1614 N/100	0 000836
0·1614 N/200	0·00115
0·1614 N/400	0·00179

TABLE V

Wave-length.	k'_{20}.	k'_{60}.	Temp. coeff.
White	0·00836	0·00157	1·87
Blue (490·5-408.5 $\mu\mu$)	0 000692	0·00130	1·88
Greenish blue (442-489·5$\mu\mu$)	0·000501	0·00103	2·05
Red (645-595 $\mu\mu$)	0·000418	0·000875	2·08

Thus the greater the initial concentration of sodium tartrate, the greater is the reaction rate whereas the greater the initial concentration of I_2, the less is the rate. It is also evident that k' is proportional directly to the square root of concentration of sodium tartrate and inversely to the square root of concentration of I_2. That with increase in the concentration of acceptor molecules, the reaction rate increases and with increase in the concentration of I_2 molecules the reaction rate decreases had also been observed in photobromination of tartaric acid by Ghosh and Basu (*loc. cit.*). Table V gives the temperature coefficients of the reaction rates under different wave-lengths of light.

CONCLUSIONS

The peculiarity of this reaction is in the large consumption of I_2 at the beginning. Whether this anomaly is due to certain photosensitive impurity which is hitherto undetected, or due to formation of certain intermediate complex, remains a subject for further investigation.

(*i*) Photoiodination of sodium tartrate is a unimolecular reaction with respect to iodine concentration. (*ii*) The monomolecular constant increases with increase of the initial concentration of sodium tartrate. (*iii*) The monomolecular constant increases with decrease of the inital concentration of iodine—an interesting peculiarity which was observed in the case of photobromination of tartaric acid by Ghosh and Basu. (*iv*) The temperature coefficient varies from 1·87 to 2·08 for different wave-lengths. (*v*) There is a progressive diminution of unimolecular constant when calculated from the first reading; but when calculated from the second, a very good unimolecular constant is obtained in all cases. This leads us to infer that large amount of I_2 is consumed at the very beginning after the reactants are mixed up by some reaction not yet known and unconnected with the main photoiodination process.

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ESTIMATION OF BISMUTH. PART IV. COLORIMETRIC ANALYSIS WITH DIMERCAPTOTHIOBIAZOLE

By Anil Kumar Majumdar

Estimation and separation of bismuth (to the extent of 3γ in 20 c.c.) from other elements have been investigated by following a colorimetric method using dimercaptothiobiazole in presence of protective colloid (gum acacia) and nitric acid. Effect of diverse ions on the colour has also been examined The peak of the absorption band of the colour system with spectrophotometre has been found to be at 470 mμ and the variation of the intensity of colour has been found to obey Beer's law at all concentrations of Bi

During his investigations on the colorimetric estimation of bismuth by thiocyanate, Mahr (*Z. anal. Chem.*, 1933, **94**, 261; 1934, **97**, 96) observed that the absorption curves of the coloured complexes of bismuth with thiourea and that with thiocyanate were practically identical. He therefore suggested a co-ordinate bond between the bismuth and the sulphur atom (*cf.* Dubsky, Okac and Okac, *Z. anorg. Chem.*, 1934, **216**, 386).

The reagent dimercaptothiobiazole (Lesanitsch, *J. Chem. Soc.*, 1922, **121**, 2544) having the reacting group N=(HS)C−S−C(SH)=N, forms with bismuth a coloured complex which, it has been shown here, can be utilised for the colorimetric estimation of the element.

Dubsky and Okac (*Z. anal. Chem.*, 1934, **96**, 267) used this reagent for the detection of small quantities of bismuth, and found the identification limit to be 1·2 μg. and sensitivity, 1 part in 28,000 parts. Ray and Gupta (*J. Indian Chem. Soc.*, 1935, **12**, 308), on the other hand, using a nitric acid solution of bismuth, and not hydrochloric acid solution, as used by Dubsky and his co-workers (*loc. cit.*), found that the identification limit could be extended to 0·1 μg. and sensitivity, to one part in 1,600,000 parts. The author (*J. Indian Chem. Soc.*, 1942, **19**, 396) however, using the reagent, has observed that if the red precipitate obtained by the reagent with the bismuth nitrate solution is peptised by a protective colloid as gum acacia, the coloration limit extends further to 1 part in 6,000,000 parts and that the colour, developed, ranging from red to yellow, depending upon the concentration of bismuth, may be used for the estimation of bismuth, even up to the extent of 3γ in 20 c.c. solution as the intensity of colour varies regularly according to Beer's law in all concentrations studied, with the help of a variable depth type colour comparator (Dubosq type). Effects of diverse ions on the colour system has also been examined.

With spectrophotometer of Schmidt and Haensch, the peak of the absorption band of the colour system has been found to be at 470 mμ and that the Beer's law is followed by the colour system has further been verified by the fact that a straight line resulted by plotting the logarithms of the observed transmittances at 470 mμ against the respective bismuth concentrations.

It is known that like hydrogen sulphide, the reagent dimercaptothiobiazole behaves as a weak acid and forms characteristic coloured precipitates with most of the metals of the H_2S group of the analytical table. With the idea of separating bismuth from these elements, the effect of organic solvents on the compounds of metals with the reagent has been examined.

EXPERIMENTAL

Reagents.—All reagents used were of 'pro analyse' variety of Schering and Kahlbaum, except the gum acacia which is of Evans Sons Lescher and Webb Ltd. (London).

Dimercaptothiobiazole ($C_2N_2S_3H_2$), m.p. 168-69°, was prepared and recrystallised by the method of Losanitsch (*loc. cit.*) and kept in an orange coloured desiccator. A solution containing 0·5% of the reagent in water was used. The solution was colourless when first prepared but slowly, on keeping over night, some yellow precipitate separated, due probably to the formation of insoluble disulphide. Solution from freshly prepared reagent was more sensitive

than the solution from the reagent prepared a few months back. This latter solution was again more sensitive than the solution kept for a week.

Bismuth.—Solutions of bismuth nitrate were prepared from sub-nitrates with water and a few c.c. of concentrated nitric acid to keep the bismuth in solution, and the bismuth contents per c.c. were determined by the oxide method (Miller and Van Dyke Cruser, *J. Amer. Chem. Soc.*, 1905, **27**, 116). From these standard solutions, solutions containing different amounts of bismuth per c.c., were prepared by dilution.

Gum acacia.—A 0·5% aqueous solution.

Nitric acid.—A normal solution of nitric acid in water.

General Procedure.—A few c.c. of the prepared bismuth solution, faintly acidic with dilute nitric acid, is taken in a tube of the Dubosq colorimeter and to that is added about 5 c.c. of N-HNO_3, a few c.c. of gum acacia solution (5 c.c.), a few c.c. water and a few drops of the reagent solution till the maximum colour is developed. The total volume of the solution is maintained at 20 c.c. During the addition of the reagent the solution is gently swirled to facilitate thorough mixing. The solution is then allowed to stand for five minutes and the colour compared. An excess of the reagent solution or the solution of gum acacia, has no influence on the colour system. If the solution contains large amounts of electrolytes, excess of gum acacia solution should be added to stabilise the colloidal suspension of the bismuth compound.

The intensity of colour has been found to increase with the increase of concentration of nitric acid. A limit of increasing intensity with the concentration of nitric acid has been observed. Intensity increased up to the conc. of 5 c.c. N-HNO_3 in a 20 c.c. soln., thereafter no further increase was observed even when the concentration of acid was extended to 10 c.c. As nitric acid hsa an influence on the colour system, it is always advisable to use the same quantity of nitric acid both for the unknown and for the standard. Even though the reagent or the gum acacia has been found to have no influence on the colour system, the same amount of them was used for the unknown and the standard as well. Results are given below:

Bi taken.	Bi found.	Error.	Bi taken.	Bi found.	Error.
1·49 mg.	1·48 mg	−0·01 mg.	0·068	0·069	+0·001
2·90	2·87	−0·03	0·01	0·01	nil
0·48	0·49	+0·01	0·003	0·003	nil
1·02	1·03	+0·01	6·48	6·43	−0·05
0·68	0·68	nil	3·888	3·90	+0·012

For the estimation of bismuth of the order of a milligram or higher, one should take the bismuth nitrate solution (containing some free nitric acid to keep the bismuth in solution) in a 100 c.c. volumetric flask, add 5-10 c.c. of normal nitric acid, a few c.c. gum sufficient to peptise the bismuth compound, dilute almost to the mark with water, add a few c.c. of the reagent solution till there is no further increase in colour, then make up to the mark with water and mix thoroughly. Colour comparison should be made, about five minutes, after the addition of the reagent, in the tubes of the comparator as usual.

Conformity to Beer's Law.—That Beer's law is followed by the colour system, through a long range of concentration of bismuth studied, is evident from the graphs given (Figs. 1—4) by plotting the reciprocal colorimetric readings on the abscissa and the concentrations on the ordinates.

FIG. 1

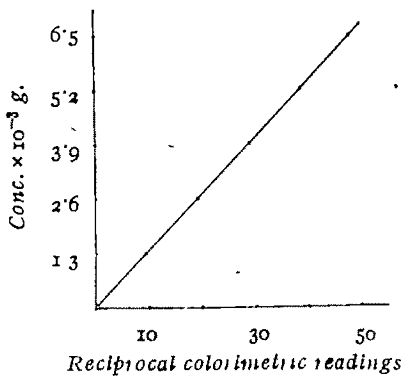


FIG. 2

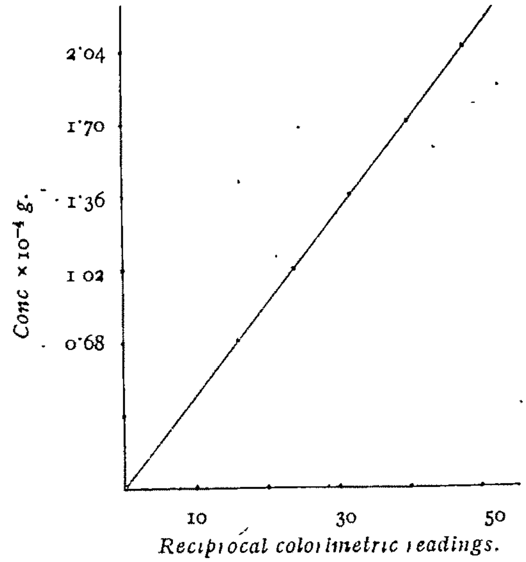


FIG. 3

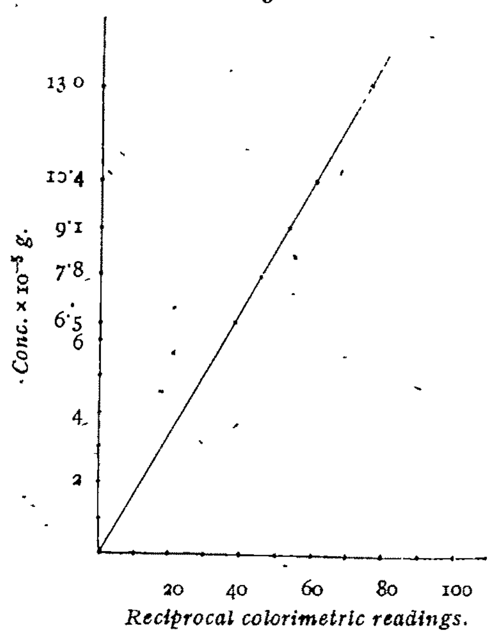
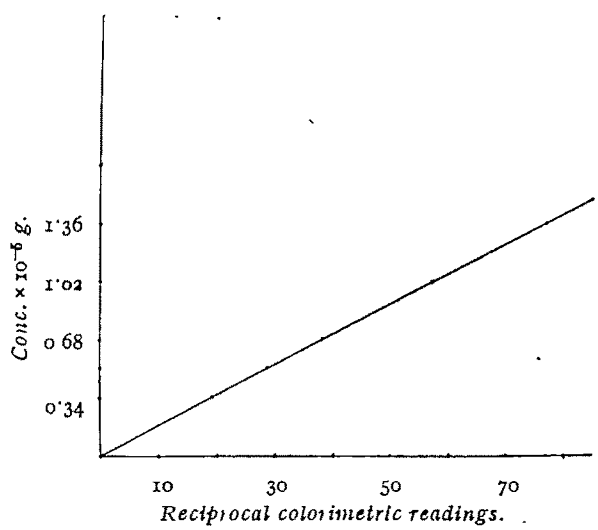


FIG 4



Stability of the Colour.—In addition to gum acacia, other substances as glycerine, agar-agar, etc. stabilise the colloidal suspension as well. A cream coloured precipitate is obtained when the reagent solution is added to the bismuth solution containing gelatine.

When the bismuth solution contains just sufficient nitric acid to prevent hydrolysis, gum acacia required to stabilise is very small in quantity, even 0·5 c.c. is found to be more than sufficient. For the same amount of nitric acid, the amount of gum acacia should be increased if the amount of bismuth is increased, and for the same amount of bismuth the amount of gum acacia should be increased, if the amount of nitric acid is increased.

The colour system keeps well without coagulation for about twelve hours when the bismuth concentration is about 10^{-4} g. or less, but with bismuth of higher concentration it keeps well for about an hour.

Interference.—To study the effects of diverse ions on the colour system, standard solutions of them were prepared from the chloride, nitrate or sulphate salts of the cations from the sodium or potassium salts of the anions. As stated earlier, a number of ions gave reactions with the reagent in neutral or acid solutions. The possible interference of a number of ions was determined under the conditions recommended in the general procedure, using bismuth concentration of 0·26 mg.

The following coloured ions interfere only if present at concentrations exceeding that required to produce the colour due to the ion itself. The limiting concentrations are : Cu^{++}, 0·07 mg.; Co^{++}, 2·5 mg.; Ni^{++}, 9 mg.

The following ions are without effect even at a concentration of : Zn^{++}, 100 mg. ; Mn^{++}, 100 mg. ; Fe^{++}, 100 mg. ; SO_4'', 100 mg. ; $C_4H_4O_6''$, 100 mg. ; 10 c.c. H_2SO_3 (saturated solution); 1 c.c. H_3PO_2 (*d.*, 1·274).

The limiting concentrations, for the interfering ions due to precipitations, are Cd^{++}, 3 mg. ; Pb^{++}, 5 mg. ; Hg^{++}, 1 mg.; Ag^{+}, 0·5 mg. ; C_2O_4'', 50 mg. ; Cl', 50 mg. ; As^{+++}, 5 mg.; Sb^{+++}, 0·2 mg. ; Sn^{++}, 1 mg. Concentration of the interfering ions can be increased if the concentration of nitric acid is increased.

In presence of phosphate ions, bismuth can be estimated by adding sufficient nitric acid to dissolve the precipitate due to phosphate. Thus by adding one c.c. excess, to that required to dissolve the precipitate, of concentrated HNO_3, bismuth is estimated in presence of 100 mg. of phosphate ions. Similarly by adding 5 c.c. of twice normal nitric acid, bismuth is determined in presence of 100 mg. of chloride or oxalate ions.

Estimation of Bismuth in presence of other Ions.—Bismuth was precipitated as phenylarsonate (Part IV of this series). Thus separated, from a number of interfering ions, the precipitate was well washed with hot water, dissolved by heating with 1 c.c. concentrated nitric acid and made up to the mark with water in a 100 c.c. volumetric flask. An aliquot part of this solution was taken in the colorimeter tube and to that were added 5 c.c. of normal nitric acid, 5 c.c. gum, diluted with water and a few drops of the reagent solution till there was no further increase in colour. Total volume of the solution was maintained at 20 c.c. The solution was thoroughly mixed and the colour compared, after standing for 5 minutes, against a standard prepared in the same way.

Results are given below.

Bi taken.	Bi found.	Bi taken.	Bi found.
0·20 mg.	0·195 mg.	0·025 mg.	0·0252 mg.
0·02	0·0196	0·0389	0·0383

Spectrophotometric study.—For the spectrophotometric studies, Schmidt and Haensch spectrophotometer was used with a cell of thickness 7·5 mm. and a spectral band width of 10 mμ. To study the wave-length of maximum absorption, 5 c.c. of the bismuth nitrate solution (0·6 mg. Bi), acidified with dilute nitric acid to keep bismuth in solution, were taken in a bottle. To this was added 11 c.c. of water, 2 c.c. gum acacia, 2 c.c. reagent and mixed thoroughly. A part of this solution was then taken in the cell and by varying the wave-length of light, the absorptions in different regions were measured. By plotting the logarithms of

the observed transmittances against wave-lengths, region of maximum absorption was found to be at 470 mμ. (Fig. 5)

FIG. 5

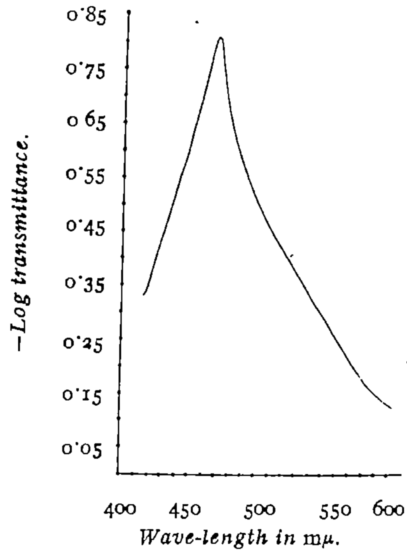
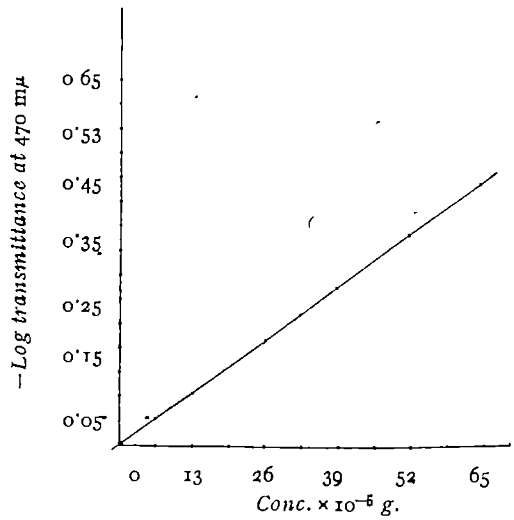


FIG. 6



Beer's Law.—That Beer's law is obeyed by this colour system, is shown by the fact that a straight line resulted when the logarithm of the observed transmittances at 470 mμ, for a number of solutions, containing from 65 p. p.m. to 650 p. p.m. of bismuth, were plotted against the respective concentrations (Fig. 6).

During the spectrophotometric studies, the reagent solution or the solution of gum acacia has been found to have no absorption in the visible region.

Solubility of the Salts formed by the Metals with the Reagent in Organic Solvents.—The bismuth compound of the reagent has been found to be soluble in alcohols, such as methyl, ethyl, propyl (normal and *iso*), *iso*amyl, and also in acetone, ethyl acetate, pyridine and ether; sparingly soluble in carbon disulphide, and insoluble in chloroform, benzene and carbon tetrachloride.

The compounds formed by lead, manganese, copper, cadmium, mercury (*ic*), cobalt and silver are insoluble in chloroform, *iso*amyl alcohol, ether and in acetone; that of nickel and zinc are soluble in acetone but insoluble in chloroform, *iso*amylalcohol and in ether; compound with tin (*ous*) is soluble in *iso*amyl alcohol, ether and in acetone but insoluble in chloroform and that of antimony is soluble in *iso*amyl alcohol and in acetone but insoluble in chloroform and in ether.

Further work on the estimation and separation of bismuth from other elements by extracting with organic solvents is in progress.

My best thanks are due to Prof. P. Rây and to Prof. J. N. Mukherjee for the facilities received in working out this piece of work in their laboratories.

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STUDIES IN THE PYRIDINE SERIES. PART IV. SYNTHESES OF SOME BASES OF THE PYRIDINE GROUP*

By Rafat Husain Siddiqui, R. H. Usmani and Syed Maqsud Ali

Diethyl 2 : 6-dimethyl-4-propyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate has been obtained by condensing ethylacetoacetate, butyric aldehyde and ammonia in presence of piperidine. The dihydro ester on oxidation in alcohol with nitrous fumes gives 2 : 6-dimethyl-4-propylpyridine-3 : 5-dicarboxylate. The potassium salt of this when distilled with soda-lime gives 2 : 6-dimethyl-4-propylpyridine, which when condensed with benzaldehyde in presence of acetic anhydride, gives 2-styryl-4-propyl-6-methylpyridine and 2 : 6-distyryl-4-propylpyridine. All the bases give well-defined crystalline salts

The object of this series of investigation is to place on record syntheses of the bases of the pyridine group and to correlate alkyl groups with reference to their positions with toxicity. The latter object has not yet been achieved. The synthesis has been effected by Hantzch's general method for pyridines as modified by Siddiqui (*J. Indian Chem. Soc.*, 1939, **16**, 410, 415). Ethylacetoacetate, butyric aldehyde and ammonia condense together in presence of piperidine to yield diethyl 2 : 6-dimethyl-4-propyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate, m.p. 125° and this gives diethyl 2:6-dimethyl-4-propylpyridine-3:5-dicarboxylate on oxidation with nitrous acid in alcoholic solution. The crude potassium salt obtained by hydrolysis of the ester with alcoholic potassium hydroxide after distillation with soda-lime gives 2 : 6-dimethyl-4-propylpyridine, b p. 193-95° and yields well defined salts. The tri-alkyl base is condensed with benzaldehyde in presence of acetic anhydride to yield 2-styryl-4-propyl-6-methylpyridine, 2 : 6-distyryl-4-propylpyridine and some unreacted base. The three bases have been separated *via* their salts (*vide* experimental). The distyryl base does not condense with bezaldehyde further and the gold complex of the base shows abnormal behaviour. The methiodides of the bases are not obtained by keeping the reactants in chloroform solution at room temperature and to obtain them in quantitative yield it is necessary to heat the solution under pressure at 100°. The monostyryl derivative on oxidation gives benzoic-acid and 2-methyl-4-propylpyridine-6-carboxylic acid. The carboxylic acid, m.p. 60° forms copper (m.p. 185-87°), ammonium and silver (m.p. 222°, decomp.) salts. The acid on decarboxylation with a trace of copper powder gives 2-methyl-4-propylpyridine which has been characterised by the picrate, m.p. 117°.

Experimental

Butyric Aldehyde.—n-Butyl alcohol (b. p. 116·8°, 300 c.c., 1·6 mol.) was oxidised by gradually adding a solution of potassium dichromate (414 g, 0·56 mol.), sulphuric acid (296 c.c., 2 mols.) in water (1420 c.c.). From the distillate on drying over sodium sulphate a fraction distilling at 70-75° was collected, yield 66 g., b. p. 73-74° (Brühl, *Annalen*, 1880, **203**, 18).

Diethyl 2 : 6-Dimethyl-4-propyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate.—A mixture of ice-cold ethyl acetoacetate (195 g., 2 mols), butyric aldehyde (54 g., 1 mol.) and piperidine (6g.) was kept at 0° for 2 hours. Dry ammonia gas (a little more than 1 mol., 13·2 g.) was passed into the mixture at 0° which then was heated in a closed flask at 100° for 4 hours. After cooling the light yellow condensate was decomposed with water when bright yellow dihydro-ester was obtained as needles (yield 165 g., 75%) After crystallisation from ethanol as pale yellow prisms it had m.p. 125°. The ester is soluble in alcohol, acetone, benzene, chloro-

* A note on an isomer of dimethylethylpyridine (*J. Indian Chem. Soc.*, 1941, **18**, 505) may be considered as Part III of this series

form, ether and ethyl acetate. (Found in material dried at 100° : C, 65·4 ; H, 8·5 ; N, 5·1. $C_{16}H_{25}O_4N$ requires C, 65·1 ; H, 8·5 ; N, 4·7 per cent).

The foregoing dihydro-ester in alcoholic suspension was oxidised with nitrous fumes till the ester dissolved in the solvent and a drop of the solution gave no turbidity with hydrochloric acid. The acid solution after making alkaline with sodium carbonate was shaken with ether. The ether solution was washed with water and dried over potassium hydroxide. The solvent was removed and the residue was extracted with petroleum ether in which the original dihydro-ester was insoluble. The unchanged ester was reoxidised. The solvent was removed and the pale yellow oily base distilled at 210° to a colourless liquid having a deep pyridine like smell (yield 60 g.). *The picrate* of the base was obtained as lemon-yellow needles from ethyl alcohol, m.p. 90-91°.

The foregoing base (60 g.) was hydrolysed with 20% alcoholic potassium hydroxide (500 c.c.) by refluxing over sand-bath for 8 hours when potassium salt separated. This as well as the residue obtained by removal of the solvent (1 part) was intimately mixed with soda lime (2 parts). The mixture after drying at 100° was distilled and the distillate was taken up in ether, the ethereal solution after washing with water was dried over potassium hydroxide. After removal of the solvent an oily base was obtained.

2 : 6-Dimethyl-4-propylpyridine distilled at 193-95° and is soluble in common organic solvents, yield 9·7 g.

The hydrochloride was obtained as yellow needles by passing hydrogen chloride into the ethereal solution of the base. It is soluble in chloroform, acetone and water.

The picrate of the base was obtained as bright yellow prisms, m p. 83° and is soluble in chloroform, alcohol, acetone, methanol, ethyl acetate and benzene but insoluble in ether and petroleum ether. [Found in anhydrous material: C, 51·1 ; H, 5·1 ; N, 14·8. $C_{10}H_{15}N.C_6H_2(NO_2)_3(OH)$ requires C, 50·8 ; H, 4·8 ; N, 14·8 per cent].

The aurichloride was obtained as bright yellow needles by adding 5% solution of gold chloride to an aqueous solution of the hydrochoride. It softens at 137° and gradually melts at 145° and is soluble in methanol, acetone and ethyl acetate. (Found in material dried at 100° : Au, 40·35. $C_{10}H_{15}N.HCl.AuCl_3$ requires Au, 40·22 per cent).

The chloroplatinate separated as dull orange coloured precipitate on adding 5% platinic chloride solution to an aqueous solution of the hydrochloride. It crystallised from alcohol as bright orange prismatic needles, m.p. 220° and is soluble in ethanol and methanol and insoluble in chloroform and acetone. [Found in substance dried at 100° : Pt, 27·36. $(C_{10}H_{15}N.HCl)_2.PtCl_4$ requires Pt, 27·48 per cent].

The Methiodide.—A solution of the base (0·5 g., 1 mol.) in chloroform and methyl iodide (0·5 g., 1·2 mol.) was left well corked overnight but no methiodide separated. This solution was therefore heated in a sealed tube at 100° for 7 hours when it turned red. On adding ether the methiodide separated quantitatively in large colourless needles, m.p. 182°. It is soluble in chloroform, acetone, ethanol and water.

Condensation of 2 : 6-Dimethyl-4-propylpyridine with Benzaldehyde.—A mixture of the base (8 g., 1 mol.), freshly distilled benzaldehyde (11·4 g, 2 mols.) and acetic anhydride (11 g, 2 mols.) was gently refluxed for 14 hours. The dark coloured condensate was acidified with 10% hydrochloric acid and distilled in steam to remove benzaldehyde. The residue was dissolved in hydrochloric acid when a clear solution (A) was obtained leaving behind a dark pasty mass. This was successively extracted with 25%, 40% and 60% glacial acetic acid and the solutions on treatment with 50% hydrochloric acid yielded identical yellow precipitates

(B) which were purified from the tarry impurities by washing with ether. The filtrate from (B) after washing with ether was mixed with (A). Nothing could be obtained from the tarry impurities contained in ether solution.

The clear yellow solution (A) was made alkaline with an aqueous solution of sodium carbonate and shaken with ether. The ether solution was washed with water and dried over anhydrous sodium sulphate and after removal of the solvent gave a light brown oily mixture of bases. The unreacted base (2 : 6-dimethyl-4-propylpyridine) distilling up to 200°, was removed and identified by conversion to the picrate, m.p. 83°. The residue distilled at 240°/740 mm. to a thick oily liquid and proved to be 2-styryl-4-propyl-6-methylpyridine.

2-Styryl-4-propyl-6-methylpyridine and its Salts.—*2-Styryl-4-propyl-6-methylpyridine* is an oily liquid possessing a characteristic pyridine like smell and could not be induced to crystallise and is soluble in common organic solvents.

The hydrochloride, obtained as sticky mass by passing dry hydrogen chloride into an ether solution of the base, crystallised from chloroform in long thin needles, m.p. 185°. It is soluble in chloroform, ethanol, acetone and water. (Found in dried material : N, 5·2 ; Cl, 12·5. $C_{17}H_{19}N$. HCl requires N, 5·1 ; Cl, 12·9 per cent). The hydrochloride on titration with bromine (1 mol.) in chloroform solution under ice-cooling gave a powder which crystallised from benzene in prisms, m.p. 168°.

The picrate, prepared from the base in ether or from the hydrochloride in acetone as a light yellow mass of needles, was recrystallised from chloroform, m.p. 225°. It is soluble in chloroform. [Found in material dried at 100° : C, 59·8 ; H, 3·9 ; N, 12·2. $C_{17}H_{19}N$. $C_6H_2(NO_2)_3OH$ requires C, 59·6 ; H, 4·1 ; N, 12·1 per cent].

The aurichloride was obtained by mixing together aqueous solutions of gold chloride and the hydrochloride as an orange coloured powder which crystallised from chloroform in thick bunches of spindle-shaped needles softening at 150° and gradually melting at 160°. It is soluble in chloroform, acetone and ethyl acetate. (Found in material dried at 100° : Au, 35·4. $C_{17}H_{19}N$. HCl. $AuCl_3$ requires Au, 35·4 per cent).

The chloroplatinate, prepared from the hydrochloride in aqueous solution as an amorphous powder, was crystallised from acetone in colourless prisms, insoluble in chloroform and ethanol, m.p. 212°. On drying *in vacuo* at 100° it suffered no loss in weight. [Found in dried material : Pt, 22·1. $(C_{17}H_{19}N.\ HCl)_2$. $PtCl_4$ requires Pt, 22·1 per cent].

The methiodide did not separate at room temperature but on warming chloroform solution of the base (1 g.) and methyl iodide (1 g.) at 70° for 2 hours a yellow powder (0·15 g.) was obtained which crystallised from chloroform-ether solution as short needles, m.p. 182-85° and unreacted base (0.75 g.) was recovered from the filtrate.

2 : 6-Distyryl-4-propylpyridine and its Salts. 2 : 6-Distyryl-4-propylpyridine.—The base from (B) was not sufficient for crystallisation and the solution in ether or chloroform showed a violet fluorescence.

The hydrochloride, prepared from the base, was crystallised from chloroform in needles, m.p. 225° and is soluble in chloroform, ethanol, methanol and acetone. (Found in material dried at 100° : N, 5·3 ; Cl, 10·0 $C_{24}H_{23}N$. HCl requires N, 5·9 ; Cl, 9·8 per cent).

The aurichloride, prepared by adding gold chloride to a solution of the hydrochloride in alcohol as an orange coloured powder, crystallised from acetone in stout spindle-

shaped needles, m.p. 190°. It is soluble in acetone and chloroform. Alcohol solution showed violet fluorescence. (Found in material dried at 100° : Au, 27·8. $C_{24}H_{23}N$. HCl. $AuCl_3$ requires Au, 29.6. $C_{24}H_{23}N$. HCl.$AuCl_3$. HCl requires Au, 28·0 per cent).

The chloroplatinate, prepared by adding an aqueous solution of platinic chloride to a solution of the hydrochloride in alcohol, was obtained as a powder, m.p. 246-48° (decomp.). It is soluble in alcohol and water. (Found in material dried at 100° : Pt, 28·4. $(C_{24}H_{23}N.HCl)_2$. $PtCl_4$ requires Pt, 28·4 per cent].

The picrate, prepared in ether solution, was crystallised from alcohol in yellow prisms, m.p. 215°. It is soluble in methanol and ethyl acetate. [Found in material dried at 100° : N, 10·3· $C_{24}H_{23}N$. $C_6H_2(NO_2)_3(OH)$ requires N, 10·0 per cent].

Oxidation of 2-Styryl-4-propyl-6-methylpyridine : Formation of 4-Propyl-6-methylpyridine-2-carboxylic Acid.—An ice-cold solution of 2-styryl-4-propyl-6-methylpyridine (1 mol., 8·6 g) in acetone (500 c.c.) was oxidised with finely powdered potassium permanganate (2 mols., 18·1 g.) added in portions during an interval of half an hour. The reaction mixture was filtered and the mud after washing with acetone was extracted with hot water. The slightly yellow aqueous filtrate, when acidified with hydrochloric acid, gave benzoic acid (2 g.). The filtrate was treated with copper carbonate (4·5 g.) when a greenish copper salt (2 g.), which crystallised from alcohol in clusters of needles, m.p 185-87°, was obtained. The filtrate gave no further yield of this salt. The copper salt was suspended in water and decomposed with hydrogen sulphide. The clear filtrate on evaporation to dryness in *vacuo* gave brownish residue (1 g.) which crystallised from ether in colourless needles, m.p. 60°.

The ammonium salt was obtained as a sticky brownish mass on passing ammonia into an ethereal solution of the acid.

The silver salt was prepared by mixing aqueous solutions of silver nitrate and the ammonium salt. It s a white powder, m.p. 222° (charring). It is soluble in alcohol and chloroform.

Decarboxylation of 4-propyl-6-methylpyridine-2-(α)-carboxylic Acid.—The acid (0·7 g.) was heated on a free flame with a trace of freshly precipitated copper powder for a few minutes when the base distilled with evolution of carbon dioxide.

2-Methyl-4-propylpyridine Picrate.—The base was converted into the picrate as bright yellow plates, m.p. 117°. It is soluble in chloroform, acetone, benzene and alcohol. (Found in material dried at 100° : C, 49·8; H, 4·5; N, 15·4. $C_9H_{13}N$. $C_6H_2(NO_2)_3(OH)$ requires C, 49·6; H, 4·4; N, 15·4 per cent).

The analyses were done by macro and micro methods.

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GLYCERIDE COMPOSITION OF TOBACCO SEED OIL

By C. Venkatarao, M. Narasingarao, and A. Venkateswarlu

The glyceride structure of tobacco seed oil has been determined by brominating the neutral oil followed by isolation of the various individual bromoglycerides by extraction with suitable solvents and estimating the fatty acid composition of these fractions The component glycerides of the oil have been found to be trilinolin (7%), oleodilinolin (35%), dioleolinolin (7%), myristodilinolin (2%), palmitodilinolin (9%), stearodilinolin (6%), myristoleolinolin (5%), palmitoleolinolin (18%), stearoleolinolin (11%). The fat conforms to the usual evenly distributed type in the structure of its component glycerides.

The glyceride structure of natural fats has been widely examined by Hilditch and his collaborators. The methods employed by them (*J. Soc. Chem. Ind.*, 1938, **57**, 44T) in the case of fats containing a high proportion of fully saturated glycerides can not be adopted for a majority of liquid fats, both animal and vegetable, containing a high percentage of triunsaturated acids. The other method of hydrogenating a fatty oil and finding the proportion of the glycerides made up wholly of stearic, oleic, linolic or linolenic acids by fractional crystallisation adopted by Hilditch and Jones (*J. Soc. Chem. Ind.*, 1934, **53**, 13T) in the case of oils containing unsaturated acids belonging to the C_{18} series such as olive, cotton seed, linseed and others of the 'non-drying', and 'drying types', does not throw any light on the association of the different unsaturated acid in the glycerides and is not found useful in the case of fish oils containing unsalurated C_{14} and C_{16} acids.

Based on the findings of Susuki and Yokoyama (*Proc. Imp. Acad. Tokyo.*, 1927, **3**, 526, 529 ; 1929, **5**, 265) Susuki and Masuda (*Proc. Imp. Acad. Tokyo*, 1927, **3**, 551 ; 1928, **4**, 165 ; 1929, **5**, 268) and Hashi (*J. Soc. Chem. Ind. Japan*, 1927, **30**, 849, 856 ; 1928, **31**, 117), Vidyarthi and Mallya (*J. Indian Chem. Soc.*, 1940, **17**, 87) evolved a quantitative method by brominating the neutral oil and separating the solid and liquid bromoglycerides into a mumber of similar fractions by extraction with suitable solvents. This method was used in adducing the glyceride structure of niger seed and safflower oil (*J. Indian Chem. Soc.*, 1940, **17**, 87 ; 1943, **20**, 45) and it was found useful in determining the component glycerides of tobacco seed oil which like niger seed and safflower oils contains palmitic, oleic and linolic acids as the major component acids and the results for tobacco seed oil have been recorded in this paper.

Experimental

Saturated Glycerides.—100 G. of tobacco seed oil, rendered neutral by treatment with sodium carbonate and filtered through decolourising carbon, were dissolved in 1000 c.c. of dry acetone and left overnight. No precipitate was obtained indicating the absence of trisaturated and disaturated glycerides in the fatty oil. This on oxidation with potassium permanganate gave a very small precipitate which was found to be mainly non-saponifiable matter.

Bromination of the Oil.—100 G. of the neutralised oil were dissolved in a litre of petroleum ether and cooled down to $-5°$. Liquid bromine was slowly added to it drop by drop maintaining the temperature at -5 to $+1°$ till the whole solution acquired a permanent brown colour. The flask together with its contents was left in ice-chest overnight when a crystalline solid was precipitated. The solid bromoglyceride was separated from the mother-liquor and further washed with chilled petroleum ether. The mother-liquor together with the washings was freed from excess of bromine by washing with dilute sodium thiosulphate solution. It was distilled and dried till free from petroleum ether. This residue obtained from the mother-liquor and the solid bromoglyceride were successively extracted with alcohol, alcohol-acetone (1:1) mixture and acetone to separate the bromoglycerides into simpler fractions as indicated in Table I.

TABLE I

- Neutral fat (100 g.)
  - Brominated fat (184 g.) in petrol ether
    - Petrol ether insoluble (26·5 g)
      - Alcohol-acetone insoluble (21·2g.) (*i*)
      - Alcohol-acetone (1·1) soluble (5·3 g.) (*ii*)
      - Alcohol soluble - nil.
    - Petrol ether soluble (158 g.)
      - Alcohol soluble (3·9g.) (*iii*)
      - Alcohol-acetone soluble (13·3 g.) (*iv*)
      - Acetone soluble (113·5 g.) (*v*)
      - Acetone insoluble (27·4 g.) (*vi*)

Debromination of the Fractions.—Each of the fractions shown in the above table was debrominated by boiling with zinc dust in a solution of methyl alcohol saturated with hydrogen chloride for nearly 2 to 3 hours, zinc dust being added in small quantities at a time till a slight excess was present. The debrominated fraction was extracted with ether and washed free of all mineral acid. It was then saponified and the mixed acids were recovered by decomposing with dilute sulphuric acid after extracting the non-saponifiable matter.

Identification of the Acids.—The individual unsaturated acids were identified by oxidising them with alkaline potassium permanganate. The saturated acids were extracted with petroleum ether from the oxidation products of these fractions and the mean molecular weights of these acids in each fraction determined. As the saturated acids from each fraction were too small in quantity to enable the separation of the individual acids, all the saturated acids of a particular fraction were considered as one acid and the saponification equivalents of these acids were used in finding the mole proportions The quantity of the individual unsaturated fatty acid in each fraction was estimated by determining the saponification equivalents, iodine values and thiocyanogen values. The analytical results are given in Table II.

TABLE II

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	Total
Wt. of bromoglycerides (g.)	21·2	5 3	3·9	13·3	113·5	27·4	184·6
Sap equivalent of acids	280·2	280·2	276·5	281 1	276·1	280·8	
I. value of acids	168·5	162·9	93·4	141·1	114·3	138·8	
Thiocyanogen value of acids	90·5	90·4	60·4	90·3	68 8	90·3	
Sap. equiv. of saturated acids	—	—	268·0	—	262·6	—	
Wt. of debrominated glyceride free from non-saponifiable matter	10·2	2·45	2·35	7·05	65·5	14·5	
Glycerides on percentage basis	10·0	2·4	2·3	6·9	64·2	14·2	
Glycerides (Mol. %)	9·9	2·37	2·3	6·8	64·6	14·0	

From the above data and the identification of individual unsaturated acids in each fraction the percentage compositions of these acids were calculated (Table III.)

TABLE III

Percentage composition of acids by weight

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	
Oleic acid	12 8	19.0	30·8	43·2	25·2	45 8	
Linolic	87·2	81·0	36·7	56·8	50·9	54·2	
Saturated acids	—	—	33·0	—	23·9	—	
Composition of acids by weight on 100 total acids							
							Total
Oleic	1·3	0·45	0·7	3·0	16·2	6 5	28·15
Linolic	8·7	1·95	0·85	3·9	32 7	7·7	55·8
Sat. acids	—	—	0·75	—	15·3	—	16·05
							100·0
Mol. per cent of the acids in the fractions on total acids.							
Oleic	1·28	0·44	0·7	2·95	15·95	6·4	27·72
Linolic	8·63	1·93	0·85	3·87	32·45	7·63	55·36
Sat. acids	—	—	0·78	—	16·17	—	16·95
							100·03

The fatty acid composition, obtained by the bromoglyceride method, agrees within experimental limits with the component fatty acids obtained by the ester fractionation method (*J. Indian Chem. Soc.*, 1943, **20**, 374).

From the above figures the component glycerides of the tobacco seed oil have been calculated and given in Table IV.

TABLE IV

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	Total
Glycerides in fractions (M %)	9·91	2·37	2·31	6·82	64·57	14·02	100·0
1. Fully sat. glyceride	nil	nil	nil	nil	nil	nil	nil
2. Disaturated glyceride	—	—	—	—	—	—	—
3. Monosaturated glyceride							
(*a*) Monosat. dilinolin	nil	nil	0·24	—	16·72	—	16·96
(*b*) Monosat. oleolinolin	nil	nil	2·07	—	31·8	—	33·87
4. Triunsaturated glyceride							
(*a*) Dioleolinolin	—	—	—	2·02	—	5 17	7·19
(*b*) Oleodilinolin	3·84	1 32	—	4·80	16·05	8·86	34·87
(*c*) Trilinolin	6·07	1·05	—	—	—	—	7·12
	9·91	2·37	2·31	6·82	64·57	14·03	

1. By the oxidation of the neutral oil with potassium permanganate in acetone.
2. By the crystallisation of the neutral oil from acetone at 0°.
3. & 4. From the component fatty acids of the brominated fractions.

All the saturated acids have been considered as one acid in the calculation of glycerides. As all the saturated acids are combined with the unsaturated acids in the form of monosaturated glycerides due to the absence of trisaturated and disaturated glycerides, the assumption that these acids are distributed proportionately in mononsaturated dilinolin and monosaturated oleolinoln will not be incorrect. From the molecular percentage of the saturated acids in the oil the component glycerides of tobacco seed oil may be given in round figures as myristoleolinolin (5%) myristodilinolin (2%), palmitoleolinolin (18%), palmitodilinolin (9%), stearoleolinolin (11%), stearodilinolin (6%), dioleolinolin (7%), oleodilinolin (35%), and trilinolin (7%).

The above glyceride structure clearly shows that tobacco seed oil adds to the list of seed fats conforming to the principle of even distribution of the fatty acids in the glyceride molecule. This oil characterised as a semi-drying oil has been found to dry best when boiled with cobalt driers and the drying property comparable to that of niger seed oil. A comprehensive study of the drying properties of the oil is in progrese.

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OBITUARY

Sir PRAFULLA CHANDRA RAY

Born: August 2, 1861. Died: June 16, 1944.

Acharya Sir Prafulla Chandra Ray, India's great scientist, philanthropist, patriot, industrialist and educationist calmly breathed his last after a brief span of illness on Friday, June 16, 1944 at 6-27 p.m. in the peaceful surroundings of the University College of Science which he had made virtually his home for the last thirty years. With Sir P. C. Ray the last of the intellectual stalwarts, who made not only Bengal but India famous throughout the world, has passed away.

Born in an ancient, cultured and aristocratic family in August 2, 1861 in the village Raruli in the district of Khulna, Bengal, Prafulla Chandra had his early education in the village school, established and run by his father, Late Harish Chandra Ray. Up to the age of nine he continued his studies there. In 1870 his father migrated to Calcutta to render better facilities of education to his sons and Prafulla Chandra was admitted to the Hare School. After four years of residence in Calcutta, a persistent attack of dysentry compelled him to discontinue his attendance at school. Parfulla Chandra had a real passion for study and this enforced stay at home gave him an ample opportunity to soar above the narrow confines of the school room and the prescribed curriculum to regale his mind with delight of studying various books in history, geography languages (including Sanskrit, Latin and French), agriculture, natural sciences, biography and contemporary scientific newspapers.

After two years of absence from the school, he joined the Albert School in 1876; his teachers there found him much ahead of his class. In 1879 he passed Entrance examination and joined the Metropolitan Institution, founded by the Late Pundit Iswar Chandra Vidyasagar, the great pioneer of advanced English education in Bengal. Though a student of the F.A. course, he became a zealous votary of science, particularly of chemistry. During his time only the Presidency College in Calcutta afforded some facilities for studies in rudimentary sciences. He took particular care to attend lectures both in chemistry and physics in the B. A. course at the Presidency College as an external student. His passion for experimental science led him to set up a miniature laboratory at the lodgings of one of his fellow students and he used to take delight in reproducing some of the experiments that were conducted in the class room. This pursuit one day landed him in difficulty and he fortunately escaped unhurt from a terrible explosion caused by a faulty apparatus.

After passing the F. A. examination in 1881, he took up the science course for the B.A. examination and also began to prepare himself for the competition of the Gilchrist Scholarship. In 1882 he secured one of the two scholarships; without completing the degree course he proceeded in the same year to England. His intention was to remain a literary student; but realising that future progress of India was interminably linked with the pursuit of scientific enquiry he chose the path of science as his immediate objective and joined in the winter session the classes preparing for the first B.Sc. examination in the Edinburgh University.

In chemistry he came under the tutelage of Prof. Alexander Crum Brown, one of the most engaging and philosophically minded professors of the modern times. In 1885 he obtained the B.Sc. degree of the Edinburgh University.

In 1888 he obtained the D.Sc. degree on his thesis in Inorganic chemistry relating to periodic classification. Hope Prize was awarded to him in the same year. He was elected for one term Vice-President of the Edinburgh University Chemical Society.

After spending full six years in Europe, Prafulla Chandra returned to India and reached Calcutta in the first week of August, 1888. He was without any appointment for a period of one year. A post of temporary Assistant Professor of Chemistry in the Presidency College on a salary of Rs 250 was offered to him ; the only inducement which actuated him to accept the post, not without chagrin, was that it afforded facilities for laboratory work for which his whole spirit hungered.

He joined the Presidency College in July, 1889 and devotoed his spare time entirely to research work for which the chemical laboratory of the Presidency College was poorly equipped at that time. His investigations in the determination of adulteration in foodstuffs, specially ghee (butter fat) and oil, extending over a period of 3 years, were published in the Journal of the Asiatic Society of Bengal in 1894. In 1896 he focussed the attention of the scientific world by his brilliant discovery of mercurous nitrite, a compound of unexpected stability. From 1897 an incessant stream of research work, either carried out by himself or in collaboration wth some of his senior students began to appear mainly in the journal of the Chemical Society, London. During the period of 1897 to 1902, he published 14 papers on the formation and stability of metallic nitrites and hyponitrites. During this period he made an important discovery that ammonium nitrite was not liable to easy decomposition as it was supposed to have been at that time and that it could be vapourised undissociated at 78°.

Soon after joining the Presidency College he established his reputation as a teacher of unusual ability. His interesting lectures, punctuated with experiments and realistic accounts from the lives of great chemists, began to weild a great influence in shaping the career of many students. He had been able to wean away some of the brilliant students, ear-marked for civil service, from the portals of Government offices to the rugged path of scientific research. By his brilliant research work in the laboratory and his inspiring lectures in the class room, he soon collected round him a band of enthusiastic young-men to carry on the research work he began ; their number multiplied as the years rolled on. From 1901 Govt. of Bengal sanctioned one stipendiary scholar to be attached to his department who during the early stage co-operated with him in his research but later on was allowed to develop his own line of research. Thus the torch of chemical research, which Sir Prafulla kindled in the laboratory of the Presidency College, began to grow in brilliancy and ultimately spread over India through the instrumentality of many of his gifted pupils who now occupy prominent position in the scientific world. And in this perhaps lies the greatest achievement of his life and devotion to the cause of chemical science.

From 1903 to 1911 he published in collaboration with his students 14 papers in the journal of the Chemical Society relating to the action of nitric acid on various metals. During 1912 to 1913, Prafulla Chandra began investigations in physical chemistry and contributed 5 papers in collaboration with Mr. N. R. Dhar (now Doctor) and with Mr. J. C. Ghosh (now Sir) in the Journal of the Chemical Society.

After a service of three decades Sir Prafulla retired from the Presidency College in 1916. His devotion to chemical research was so deep that when he was once offered principalship of the Rajshahi College (Bengal) with higher emolument and in the superior grade of Educa-

tional service; he point-blank turned down the offer as it entailed no research facilities. After his retirement from the Presidency College he found a more congenial atmosphere of research as the Palit Professor of Chemistry in the University College of Science, founded by Late Sir Asutosh Mukherjee with the princely endowments of Sir Rash Behari Ghosh and Sir Tarak Nath Palit. He occupied the chair from 1916-1937 and during this time he carried out numerous investigations on varying valency of gold and platinum, chelate compounds, organo-metallic derivatives and mercaptans in collaboration with his students. Sir Prafulla finally retired from the chair in 1937 and was made Emeritus Professor uptil his death. During his active life he in collaboration with his students contributed no less than 142 papers in the journals of the Chemical Society, London and the Indian Chemical Society, Zeitcshrift für anorganische Chemie and Annales de chimi-physique.

On completion of his 60th year in 1922, Sir P. C. Ray signified his intention of vacating the Palit Chair ; at the request of the Senate he continued to occupy the post for 5 years more but he expressed his intention that from that date his whole salary should be utilised for the furtherance of chemical research and for the development of the Chemistry Department of the University College of Science. Since his retirement in 1937 his accumulated salary from 1922 to 1937 amounted to nearly 2 lakhs of rupees and the amount has been funded as an endowment for two research scholarships in chemistry.

The school of chemistry, which he formed as a nucleus at the dawn of this century, gradually flourished at his inspiration and ultimately found its consummation in the establishment in 1924 of a national organisation of chemists in India, known as the Indian Chemical Society, and a national journal of chemists, the Journal of the Indian Chemical Society which has established its reputation in the scientific world. Sir P. C. Ray was elected as its Foundation President and held the office for two successive terms. He made a generous donation of Rs. 12,000 to the funds of the Society. The Society celebrated his 70th Birthday in a fitting manner and presented to him on the occasion a special volume of its journal, "Sir P. C. Ray 70th Birthday Commemoration Volume" to which the celebrated chemists of Europe and America, besides those of India, contributed their original research memoirs. To commemorate his 70th Birthday, Dr. S. S. Bhatnagar (now Sir) awarded for some years (under the auspices of the Society) a gold medal to young chemists for best papers published in the Journal of the Indian Chemical Society. During the celebration of his 80th Birthday, organised by the University of Calcutta, the Society presented to him an address in a silver casket.

It is no wonder that there is hardly an eminent chemist in India now who does not owe his fame to the inspiration of this great Indian savant. By founding the national organisation of chemists he has rendered a signal service to the cause of chemistry in India and it will be recalled as a glorious land-mark in our national progress.

Acharya Prafulla Chandra is no more but his name will be immortalised as a path-finder and originator of work of great utility. In his long and distinguished career as a research worker he had evoked a true spirit of scientific enquiry among his many disciples which has resulted in the creation of the flourishing school of chemistry that we see in India to-day. Such an achievement in the life-time of one man is remarkable indeed.

He was one of the first to realise the importance of Indian industries for the economic advancement of the country. He was so much imbued with the idea that soon after he got

an appointment, he risked the very little fund that he could spare in the venture. The nucleus of a chemical industry, which he started in the midst of his fundamental researches in 1893 under the name of the Bengal Chemical & Pharmaceutical Works, as a private firm at 91, Upper Circular Road, has now thrived into perhaps one of the most successful and biggest chemical concerns in India under his fostering care. In 1902 it was made a limited concern with a capital of 2 lakhs of rupees. At the present time its asset amounts to half a crore of rupees and its sulphuric acid plant is recognised to be the biggest of its type in Asia. The Bengal Chemical & Pharmaceutical Works is a remarkable creation of Sir P. C. Ray's industrial genius providing employment to many thousands of workers. He was also intimately connected in promoting other industrial concerns of varied type.

He was an industrialist, yet in body and spirit he was quite distinct from what the common term implies. In establishing all the industries he was never actuated by any personal financial gain. He put his energy and time for the industrial development of India ; he never drew any dividend for himself but he spent the entire amount for national and philanthropic purposes.

Sir P. C. Ray was a chemist by choice; science had been his preoccupation for over 60 years. From his tender age Prafulla Chandra had a penchant for history and literature which he tried to suppress at Edinburgh. While a student of the B.Sc. class of the Edinburgh University, he made time from his routine work to compete for a prize announced by the then Lord Rector of the University for the best essay on "India before and after mutiny". His essay came out second best, and was highly spoken of by the contemporary English periodicals. To the same penchant have come out such books and pamphlets like "The misuse of Bengali brain", "Endeavour and success", "Essays and discourses", and numerous articles and papers. To his leaning towards history and literatutre, particularly towards History of Chemistry, we owe his monumental work on "History of Hindu Chemistry" (in two volumes). Inspired by Berthelot's three monumental volumes on "Syriac, Arabic and Middle Age Alchemy" which he had sent to Sir P. C. Ray as a token of his (Berthelot's) appreciation of Sir P. C. Ray's essay on Hindu chemistry, Sir P. C. Ray threw himself in right earnest in the midst of research work in writing a history of Hindu Chemistry, the first volume of which appeared in 1902 and the second in 1908. These two volumes are considered to be a work of great erudition and have unfurled before the world the cultural heritage of India. In 1932 he published the first volume of his autobiography "Life and Experiences of a Bengali Chemist" and the second volume in 1937. In the words of Dr. H. E. Armstrong "from the beginning to end the message of the book is one of highest endeavour—pulsating with vitality and intellectual force." The book has been dedicated to the youths in whom he wanted to live for ever.

In 1904 for the second time he visited Europe on a deputation by the Govt. of Bengal. In 1912 he revisited England as a representative of the University of Calcutta to the Empire University Congress. Honorary degree of D. Sc. was awarded to him in 1912 by the University of Durham, and also by the Universities of Calcutta, Dacca and Benares. He was decorated with C. I. E. in 1911 and knighted in 1917. He made his fourth visit to Europe in 1920 and in the same year he was elected General President of the Indian Science Congress. He made his last visit to Europe in 1926 as a delegate to the 3rd session of the Congress of the Empire Universities. In 1934 he was elected Honorary Fellow of the Chemical Society, London. Sometime earlier he was elected Honorary member of the Deutsche Akademie, München.

Sir P. C. Ray was a chemist by profession and an industrialist by inclination ; but his heart always remained with the people and the country. True spirit of nationalism pulsated through every fibre of his brain and body. He has served his country with head and heart. His head was big but his heart was bigger. Though Acharya Ray achieved fame far and wide as a great teacher, chemist, research worker and an exponent of industries, but his name is more familiar throughout India as a true philanthropist, patriot and social worker. He gave away his all for the poor and suffering humanity. Whenever natural calamities devastated any district of Bengal, he was always ready to relieve the distress of the srricken hnmanity by organising relief centres. He claimed so much faith and esteem of his countrymen that whenever he appealed for funds, money simply flowed to him for the relief purpose. The Bengal Famine Relief Committee, Khulna Famine Relief Committe, and Sankat Tran Samity organised by him on the occasion of Khulna famine (1921) and North Bengal Flood (1922) will be ever cherished as his glorious service for the stricken humanity. His purse remained always open for the poor students. In later years his charities stepped beyond the circle of students on to the larger world outside. He made over a large number of his share scrips worth at present at Rs 70,000 to a Trust with a view to benefitting poor widows, orphans and to propagating hand-spinning and production of *Khaddar.*

Sir P. C. Ray was a great patriot : he symbolised the true spirit of nationalism. When the clarion call came for any nationalistic movement he never lagged behind any one, he came out of his laboratory and threw himself head and shoulder in it. During the Rowlatt Act Agitation in 1919 he was with Late Mr. C. R. Das and declared in the Town Hall meeting that though he was a man of the laboratory—"If there were occasions that demanded that, he should leave his test-tube to attend the call of the country..." Neither was he in the background during the upheaval of the great non-co-operation movement which Mahatma Gandhi led in 1929. He swam right through it in dead earnest. He took to spinning and kept it regularly as a religious practice till his vision began to fail. He never used any clothing which was not made of *Khaddar* till the end of his life. His body was frail and fragile but it contained wlthin it a virile and dynamic personality and fostered a spirit which acted as a veritable power house providing limitless energy which his many-sided activities for all spheres of human interest demanded. Intellectual, scientific and industrial and economic advancement, social reform and political freedom, all made simultaneous appeal to him and absorbed as much time and service as his laboratory work and teaching demanded.

His wants were few ; his personal habits exemplified Spartan simplicity. He was great but he never felt it. Despite his English training he had remained absolutely oriental in habits and tastes and always lived in realisation in spirit and practice of that rare combination of plain living and high thinking of the ancient vedic *Gurus*. The most outstanding feature of his greatness was his love for the people. Though much above the common level, Sir P. C. Ray identified himself with the common man and in his service for the people he gave himself without stint and to quote Late Sir J.C. Bose "The combination of such qualities in a single individual is indeed rare in any country, and there can be no higher example for the young generation to emulate than the life of this great teacher".

An account of papers published by Sir P. C. Ray (marked with an asterisk) and with his students

* 1. Conjugated sulphates and isomorphous mixtures of the copper-magnesium group (*Proc. Chem. Soc.*, 1897, p. 53).

* 2. Nitrites of mercury and the varying conditions under which they are formed (*J. C. S.*, 1897, **71**, 337).

* 3. Mercury hyponitrites (*J. C. S.*, 1897, **71**, 348).

* 4. Interaction of mercurous nitrite and the alkyl iodides (*Proc. Chem. Soc.*, 1896, p. 218).

* 5. Mercurous nitrite (*Z anorg Chem.*, 1896, **12**, 365).

* 6. On the action of sodium hyponitrite on mercuric solutions (*J. C. S.*, 1897, **71**, 1097).

* 7. On the interaction of mercurous and mercuric nitrites of silver and sodium (*Proc. Chem. Soc.*, 1899, p. 103).

* 8. On a new method of preparing mercuric hyponitrite (*J. C S*, 1897, **71**, 1105).

* 9. Interaction of mercurous nitrite and ethyl iodide (*Proc. Chem. Soc*, 1899, p. 239).

* 10. Mercurous iodide (*Proc Chem. Soc.*, 1899, p. 239).

* 11. A new series of dimercuriammonium salts (*Proc. Chem. Soc.*, 1901, p. 96).

* 12. Dimercuriammonium nitrite and its haloid derivatives (*Proc Chem. Soc.*, 1901, p. 96; *J. C. S.*, 1902, **81**, 664).

* 13. Determination of adulteration in foodstuffs (*J. Asiatic Soc. Bengal*, 1894, **59**, 63).

14. Piperizinium nitrite (*ibid.*, 1912, **8**, 107).

* 15. Dimercuriammonium nitrate (*Ann chim. phys.*, 1903, **72**, 215).

* 16. Mercuric nitrite and its decomposition by heat (*J. C. S.*, 1904, **85**, 523).

* 17. Theory of the production of mercurous nitrite and of its conversion into various mercury nitrates (*J. C. S*, 1905, **87**, 171).

* 18 The nitrites of the alkali metals and metals of the alkaline earths and their decomposition (*J C. S.*, 1905, **87**, 177).

* 19. The sulphate and the phosphates of the dimercuriammonium series (*J. C S.*, 1905, **87**, 9).

* 20. Mercurous hyponitrite (*J. C S*, 1907, **91**, 1404).

* 21 Cupric nitrite (*J. C. S.*, 1907, **91**, 1405).

* 22. Double nitrites of mercury and the alkali metals (*J. C S*, 1907, **91**, 2031).

* 23. Silver mercuroso-mercuric oxynitrates and the isomorphous replacement of univalent mercury by silver (*J. C. S.*, 1907, **91**, 2033).

* 24. Molecular volumes of the nitrites of silver, mercury and the alkali metals (*J. C S.*, 1908, **93**, 997)

* 25. Lithium nitrite and its decomposition by heat (*Proc. Chem. Soc.*, 1908, p 75)

* 26. Molecular volumes of nitrites of Ba, Sr, and Ca (*J. C S.*, 1909, **95**, 66)

* 27. Decomposition and sublimation of ammonium nitrite (*J. C. S*, 1909, **95**, 345).

* 28. Double nitrites of mercury and the metals of the alkaline earths (*J. C. S.*, 1910, **97**, 326)

* 29. Double nitrites of mercury and the bases of the tetra-alkylammonium series (*Proc. Chem. Soc.*, 1910, p. 172).

* 30. Influence of minute quantities of ferric salts and of manganese nitrate on the rate of solution of mercury in nitric acid (*J. C S*, 1911, **99**, 1012).

* 31. Nitrites of the benzylammonium series (*J. C S.*, 1911, **99**, 1475)

32. Benzylmethyl, benzylethyl and allylammonium nitrites (*Proc. Chem. Soc*, 1912, p 258)

33. Isomeric allylamines (*J. Asiatic Soc. Bengal*, 1912, **8**, 103).

34 Molecular conductivities of potassium nitrite, mercuric nitrite and potassium mercurinitrite (*J C. S.*, 1912, **101**, 965).

35-37. Chlorides of mercurialkyl and mercurialkylaryl ammonium series and their constitution as based on conductivity measurements (*Proc. Chem. Soc.*, 1912, p 292; *J C. S.*, 1913, **103**, 3, 101)

38. Molecular conductivity and ionisation of nitrites (*ibid.*, 1912, p. 319)

39. Vapour density of ammonium nitrite (*J C. S.*, 1912, **103**, 1185).

40-41. Nitrites of the mercurialkyl and mercurialkylarylammonium series (*J. C. S*, 1912, **101**, 616, 1552).

42. Constitution of nitrites. Two varieties of silver nitrite (*Proc. Chem. Soc.*, 1905, p 278).

43. Fischer's salt and its decomposition by heat (*J. C. S*, 1906, **89**, 551).

44 Decomposition of mercurous and silver hyponitrites by heat (*J. C. S.*, 1907, **91**, 1399).

45. Decomposition of hyponitrous acid in presence of mineral acids (*ibid.*, 1907, **91**, 1866).

46. Decomposition of ammonium platinichloride and bromide by heat (*Z. anorg. Chem.*, 1909, **64**, 184).
47. Decomposition of dimercuriammonium nitrite by heat (*J. C. S.*, 1910, **97**, 323).
48. Ionisation of the nitrites as measured by the cryoscopic method (*Proc. Chem. Soc.*, 1910, p. 173).
49. Interaction of the alkylsulphates with nitrites of the alkali metals and metals of the alkaline earths (*J. C. S.*, 1906, **89**, 1900).
50. Preparation of aliphatic nitro compounds by the interaction of the alkyl iodides and mercurous nitrite (*Proc. Chem. Soc.*, 1907, p. 246).
51. Methylammonium nitrite (*J. C. S.*, 1911, **99**, 1016).
52-55. Nitrites of the alkylammonium bases (*ibid.*, 1911, **99**, 1470; 1912, **101**, 141, 216, 612).
56. Trimercuridiethylammonium nitrite (*J. C. S.*, 1911, **99**, 1972).
57. Nitrites of the alicyclic ammonium series (*Proc. Chem. Soc.*, 1912, p. 102)
58. Decomposition of mercurous nitrite by heat (*J. C. S.*, 1903, **83**, 491).
59. Tetramethylammonium hyponitrite and its decomposition by heat (*J. C. S.*, 1911, **99**, 1466).
* 60. Additive and substitutive compounds of mercuric nitrite with organic thio derivatives (*Proc. Chem. Soc.*, 1914, p. 140).
* 61. Action of mercuric, cupric and platinic chlorides on organic sulphur compounds (*Proc. Chem. Soc.*, 1914, p. 304).
* 62. Action of nitrous acid on dimethylpiperizine (*ibid.*, 1914, p. 143).
* 63. Place of mercury in the periodic system (*Chem News*, 1914, **109**, 85).
* 64. Interaction of dimercuriammonium nitrite and the alkyl iodides (*J. C. S.*, 1915, **107**, 125).
* 65-68. Mercury mercaptide nitrites and their reactions with the alkyl iodides (*J. C. S.*, 1916, **109**, 131, 603; 1917, **111**, 101, 1919, **115**, 548).
* 69. Cadmium and zinc nitrites (*J. C. S.*, 1917, **111**, 159).
70. Alkylammonium nitrite (*J. Asiatic Soc. Bengal*, 1912, **8**, 101).
* 71. Alkaloidal derivatives of mercuric nitrite (*J. C. S.*, 1917, **111**, 507)
* 72. Interaction of mercuric and cupric chlorides respectively with the mercaptans and potential mercaptans (*J. C. S.*, 1919, **115**, 871).
* 73-74. Triethylene tri- and tetra-sulphides (*J. C. S.*, 1920, **117**, 1090; 1922, **121**, 1279).
75. Chloropicrin as a reagent for the diagnosis of mercaptans and potential mercaptans (*J. C. S.*, 1922, **121**, 323).
76. Molecular volumes of the hyponitrites of the alkali metals and metals of the alkaline earths (*J. C. S*, 1916, **109**, 122).
77. Isomeric allylamines (*J. Asiatic Soc. Bengal*, 1912, **8**, 371).
78. Equivalent conductivities of Na and Ca hyponitrites and hyponitrous acid (*J. C. S.*, 1913, **103**, 1562).
79. Interaction of iodine and thioacetamide in aq. and alcoholic solutions (*J. C S.*, 1916, **109**, 698).
80. Synthesis of $\alpha\beta$-thiocrotonic acid (*J. C. S.*, 1917, 111, 510).
81. Velocity of decomposition and the dissociation constant of nitrous acid (*J. C. S.*, 1917, **111**, 417).
82. Guanidinium nitrite and its decomposition by heat (*J. C. S.*, 1913, **103**, 283).
83. Action of monochloroacetic acid on thiocarbamides and monoalkylated thiocarbamides (*J.C.S.*, 1914, **105**, 2159).
84-86. Mercury mercaptide nitrites and their reaction with alkyl iodides (*J.C.S.*, 1919, **115**, 261, 541, 1148).
87. Reaction of potassium salts of 2-thiol-5-thio-4-phenyl-4.5-dihydro-1:3:4-thiodiazole and 2:5-dithiol-1:3:4-thiodiazole with halogenated organic compounds (*J.C.S.*, 1919, **115**, 1308).
88. Vapour density of ammonium nitrate, benzoate and acetate (*J.C.S.*, 1913, **103**, 1565).
89. Molecular conductivity of some sulphonium compounds in acetone (*J.C.S.*, 1921, **119**, 1643).
90. Nitrites of the alicyclic ammonium series *J.C.S*, 1913, **103**, 1).
91. Mercuric sulpho-oxychloride (*J.C.S.*, 1919, **115**, 552).
92. Synthesis of cyclic polysulphides (*J C.S*, 1924, **125**, 1141).
* 93 Varying valency of platinum with respect to mercaptanic radicles (*J.C.S.*, 1923, **123**, 133).
* 94-95. Triethylene tri-and tetrasulphides (*J.C.S.*, 1923, **123**, 2147; 1922, **121**, 1279).
96. Mercaptans of the purine group (*J.C.S.*, 1923, **123**, 1957).
97-102. Varying valency of platinum with respect to mercaptanic radicles (*J. Indian Chem. Soc.*, 1925, **2**, 178; 1926, **3**, 155, 358; 1927, **4**, 467; 1928, **5**, 139; 1934, **11**, 737).

* 103. Varying valency of gold with respect to mercaptanic radicles (*J. Indian Chem. Soc.*, 1924, **1**, 63).
* 104. Oxidation of triethylene tetrasulphide by means of $KMnO_4$ (*J.C.S*, 1925, 208).
* 105. History of oxygen (*J Ind. Chem. Soc.*, 1926, **3**, 1).
106 Triethylene trisulphide and 1:4-dithian (*J.I.C.S.*, 1926, **3**, 73).
107. Lengthened chain compounds of sulphur (*ibid.*, 1926, **3**, 75).
108. Synthesis of condensed heterocyclic systems Interaction between 2:5-dithiol-1:5:4-thiodiazine and organic dihalides (*J.I.C S.*, 1926, **3**, 23).
109-110. Double sulphates of the copper-magnesium group and the sulphonium bases (*J I.C.S.*, 1927, **4**, 37; 1928, **5**, 69).
* 111. On the variability of valency (*J I C S.*, 1927, **4**, 89).
112. Complex compounds of gold with mercaptanic, radicles (*J.I.C.S.*, 1928, **5**, 527).
* 113. Isomorphism and homology (*Nature*, 1929, **124**, 480).
114-119. New type of complex platinum compounds. Ter and quinque-valent platinum (*Z. anorg. Chem.*, 1929, **178**, 329; 1930, **187**, 33; 1933, **211**, 62; 1934, **220**, 24; 1931, **198**, 53; 1932, **203**, 406).
120 Tetraethylphosphonium nitrite (*J.I.C S*, 1928, **5**, 733).
121. Double sulphates of the copper-magnesium group and the phosphonium bases (*J.I C.S.*, 1929, **6**, 27).
122. Action of bases on complex compounds derived from organic thio compounds and platinic chloride (*J.I.C S.*, 1929, **6**, 885).
123. Synthesis of lengthened sulphur chain compounds (*J.I.C.S.*, 1929, **6**, 865).
* 124. Chemical elements and compounds (*J.I.C.S.*, 1933, **7**, 1).
* 125. Isomorphism and chemical homology (*Nature*, 1930, **126**, 310).
126. Complexes of mercuric iodide with alkyl sulphonium iodides (*J.I.C.S.*, 1930, **7**, 297).
127. Complex compounds of chloro-ferric acid with organic sulphur compounds (*Z. anorg. Chem.*, 1930, **187**, 121).
128. Complexes of gold chlorides with organic sulphides (*J.I.C.S.*, 1930, **7**, 67).
129. Compounds of metallic salts with organic sulphides (*J.I.C.S.*, 1931, **8**, 537)
130. Complexes of antimony trichloride with organic sulphides (*ibid*, 1931, **8**, 711).
131. Complexes of antimony halides with sulphonium halides (*ibid*; 1931, **8**, 287)
132. Studies on the reactions of silver nitrate with organic sulphides (*ibid.*, 1931, **8**, 689).
133. Complexes of zinc and cadmium iodide with alkyl sulphonium iodides (*ibid.*, 1931, **8**, 739).
134-137. Complex compounds of iridium (*J.I.C.S.*, 1932, **9**, 251; 1933, **10**, 275, 1934, **11**, 51; 1936, **13**, 138).
138. Thioketonic esters (*ibid*. 1933, **10**, 75).
139-141. Fluorination of organic compounds (*Nature*, 1933, **132**, 749; *J.I.C.S.*, 1935, **12**, 93; 1936, **13**, 427).
142. Synthesis of thiocamphor and other cyclic thioketones (*Nature*, 1934, **134**, 1010)

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STUDIES IN THE SANTALOL SERIES. PART I.

SEPARATION OF THE SANTALOLS AND THE SANTALENES

BY P. C. GUHA AND S. C. BHATTACHARYYA

The alcohols, α-and β-santalols have been isolated from East Indian sandalwood oil and their physical constants determined. The process has been treated mathematically and several graphs and tables drawn in this connection furnish now an easy method of finding out the composition of a sample of sandalwood oil. Both α-and β-santalene of a high degree of purity have also been obtained and the probable optical rotations of the pure compounds determined by mathematical calculations.

East Indian sandalwood oil, which is obtained from the heart of wood of *Santalum album*, contains near about fourteen chemical substances comprising alcohols, aldehydes, ketones, hydrocarbons, etc. (Simonsen, "Terpene." Vol. II, p. 544). The main bulk of the oil comprises two sesquiterpene primary alcohols ($C_{15}H_{24}O$), α-and β-santalols, and in fact they form almost the entire amount of the higher boiling fraction of the oil. The main constituents of the lower boiling fractions are two isomeric sesquiterpenes ($C_{15}H_{24}$), α-santalene and β-santalene. The other ingredients *viz.* acids, aldehydes, etc. form only a comparatively minor part (*cf.* Parts IV and V of this series).

It has been established through the classical researches of Semmler (*Ber.*, 1910, **43**, 1893), Ruzicka (*Helv. Chim. Acta*, 1935, **18**, 355) and Simonsen (*J. Chem. Soc.*, 1935, 309) that both α-santalol and α-santalene are tricyclic compounds possessing a long side-chain and an ethylenic linkage ; whereas the corresponding β-compounds are bicyclic, containing two double bonds in their molecules.

The acidic, aldehydic and ketonic ingredients can be easily separated in the form of their derivatives. The separation of the main constituents of sandalwood oil *viz.* the two santalols and the two santalenes is, however, attended with difficulties and could not be successfully effected by earlier workers (Schimmel & Co. Report, 1910, Oct., p.113 ; Semmler, *Ber.*, 1910, 43, 445 ; Paolini and Divizia, *Atti. R. Acad. Lincei*, 1914, **23**, 226).

The Hydrocarbons.

The boiling points of α-and β-santalene lie close to each other, the former boiling at 118°/7 mm. and the latter at 127° under the same pressure. The difficulty in separation is further augmented by the similarity of their general characteristics and when they are distilled, one comes invariably mixed up with the other isomeride. Moreover, β-santalene is a highly *l*-rotatory compound, whereas the α-isomeride has been shown by us to possess a feeble *d*-rotation (according to previous workers it is slightly *l*-rotatory, Schimmel & Co., *loc. cit.*). Evidently, even a trace of the highly *laevo*-rotatory β-compound affects the optical purity of its α-isomeride to a great extent and *vice versa.*

Alcohols.

What has been described about the properties of the hydrocarbons hold equally well in the case of the alcohols. Thus α-santalol is a feebly *d*-rotatory compound, b.p. 148°/5 mm. and the corresponding β-isomeride is a highly *l*-rotatory compound, b.p. 158°/5 mm.

Recently Simonsen has isolated the santalols (Simonsen, *loc. cit.*) in a pure state by repeated fractionations and has determined their physical properties, but, unfortunately, no exhaustive description is made about the details of this important separation. As we were in need of some pure α-santalol for comparison with our synthetic variety, we had to undertake the problem of separation of the two santalols as also of the two santalenes.

The separation of the santalenes is rendered even more difficult due to their presence in very small quantities (only 4 to 6%) in the sandalwood oil. Anyway, by repeated fractionations through two special types of fractionating columns, it has been possible to isolate α-and β-santalol in a state of absolute purity and their physical constants have been determined. As one of the Indian States (Mysore) at present commands the major supply of this commodity, the whole process has been exhaustively treated. Several graphs and tables drawn in this connection, by way of correlating the quantities of their ingredients with the unsaturation number and the corresponding optical rotations, furnish now an easy and a mechanical method of determining the composition of a santalol mixture in a more or less correct measure.

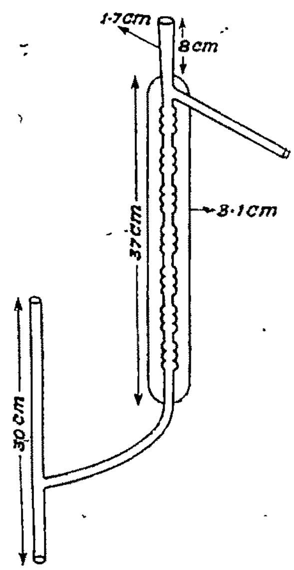
Samples of α-and β-santalene of about 90% purity have also been isolated. As the amount of substance at our disposal was not quite adequate, further purification beyond this limit was not possible; but our samples were purer than the samples of the hydrocarbons isolated by earlier workers. It has also been possible to determine the probable optical rotations of pure α- and β-santalene with the help of some mathematical calculations.

The course of separation was followed by a polarimeter and by measuring the amount of unsaturation with percamphoric acid (Milas and McAlevy, *J. Amer. Chem. Soc.*, 1933, **55**, 349). Obviously the pure β-compound will have an unsaturation value of "Two", whereas that for the α-compound will be "One". By this method, the composition of a santalol or santalene mixture could be determined to a degree of reasonable accuracy.

For the actual process of separation two columns were used, one of which (No. 1) has been devised by Bradfield (*J. Soc. Chem. Ind.*, 1935, **54**, 6T) and the other (No. 2) by us. The first one was primarily used in the case of the santalols and for the earlier fractionations of the santalenes; the final stages of the separation of these hydrocarbons being carried with the help of the second column. The special features of the columns are the outer jackets. In each case the space between the outer jacket and the inner tube was evacuated with the mercury diffusion pump to 10^{-6} mm. of mercury and sealed properly. The introduction of an outer jacket serves the purpose of a thermos flask and reduces the transference of heat due to

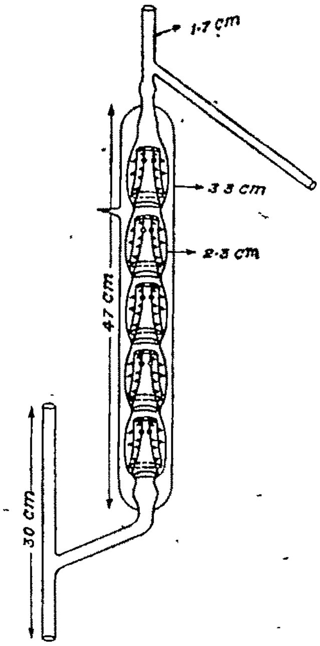
radiation to a minimum. The column No. 1 is particularly suitable for the fractionation of viscous liquids like the sesquiterpene alcohols; whereas the second one is

FIG. 1.



No. 1.

FIG. 2.



No. 2.

more effective for the fractionation of the less viscous and comparatively low boiling compounds like the hydrocarbons.

The rate of distillation was so regulated that only one drop of liquid distilled per second. For maintaining an inert atmosphere and particularly for facilitation of the stirring of the liquids, dry and pure carbon dioxide was drawn through the liquid under treatment. A metal-bath was used as the source of heat. The method of treatment which has been followed in this paper is expected to be helpful in the case of separation of ingredients of other essential oils. The fractionating columns used in this investigation may also be useful in other difficult separations.

EXPERIMENTAL

A sample of Government-certified sandalwood oil from the Mysore Sandalwood Oil Factory was saponified by boiling for ½ hour with 3% alcoholic potash solution. The oil was precipitated by pouring into excess of water, extracted with ether and washed thoroughly with water to remove the last trace of alkali. After drying and removal of ether, the residual oil was subjected to vacuum distillation under 5 mm. pressure and divided into two fractions. The lower boiling fraction contained the santalenes and the higher boiling fraction contained the santalols. The two fractions were then further subdivided as shown below :

Alkali-treated oil

- Fraction A — b. p. up to 140°/5 mm. mainly santalenes
  - Fraction A_1 — b. p. up to 118°/5 mm. mainly α-santalene.
  - Fraction A_2 — b p, 118-140°/5 mm. mainly β-santalene,
- Fraction B — b. p. above 140°/5 mm. mainly santalols
  - Fraction B_1 — b. p. up to 152°/5 mm mainly α-santalol.
  - Fraction B_2 — b. p. above 152°/5 mm. contains β-santalol.

All the fractions A_1, A_2, B_1, B_2, were then repeatedly fractionated for the isolation of the pure substances and will be described separately and individually.

Isolation of α-Santalol.

Fraction B_1 was repeatedly fractionated at 5 mm. pressure and the portion coming just at 147-148°/6 mm. was collected ; anything coming above and below this temperature being collected separately.

The gradually changing unsaturation numbers and the corresponding optical rotations of the same fraction, distilled repeatedly at 147-148°/5 mm. for 21 times, have been shown in Table I. It is evident that in the case of the santalols a constant boiling point does not necessarily mean that the distillates are identical.

The results have also been plotted graphically (Fig 3).

TABLE I

No of distilation.	Observed rotation in degrees α5780.	Observed unsaturation number.	No. of distillation.	Observed rotation in degrees α5780	Observed unsaturation number.
1	− 16·8	1 285	12	+4·0	1·05
2	− 13·8	1·245	13	+4·8	...
3	− 11·0	...	14	+5·4	...
4	− 9·5	1·20	15	+6 1	1 02
5	− 6·1	...	16	+6·62	...
6	− 3·0	1 13	17	+7·2	1·01
7	− 1·2	...	18	+7·8	...
8	0 0	...	19	+8 31	...
9	+ 1·0	1·08	20	+8 79	...
10	+ 2·1	...	21	+9·02	1·00
11	+ 3·15	...			

The two santalols show a tendency of coming over as a constant boiling mixture at 152°/5 mm. Great care should, therefore, be taken during the earlier period of fractionations.

The proportion of α- and β-santalol, in any arbitrary mixture, was calculated from the corresponding uusaturation number with the help of the following simple algebraic calculations :

Let in any mixture, percentage of α-santalol be x,

Therefore, percentage of β-santalol should be $100-x$.

Now a β-santalol molecule contains two double bonds and α-santalol molecule contains one double bond.

Therefore, the total amount of unsaturation is proportional to $x \times 1 + (100-x)2$.

Therefore, the average unsaturation value which may be determined with percamphoric acid

$$U = \frac{x \times 1 + (100-x)2}{x + 100 - x}.$$

On simplification x (percentage of α-santalol) $= 200 - U$.

Percentage of β-sanralol is obained by difference.

The results correlating the relation between the unsaturation number and percentage of α-santalol-rich mixture have been shown in Table II.

TABLE II

No.	Unsaturation number.	α5780.	Percentage unsaturation.	of α-Santalol from rotation.	Percentage unsaturation.	of β-Santalol from rotation.
1	1·285	−16·8	71·5	69·6	28·5	30·4
2	1·245	−13·8	75·5	73 11	24·5	26·8·9
3	1·20	− 9·5	80·0	78·16	20·0	21·85
4	1·131	− 3·0	86·9	85·79	13·1	14 21
5	1·08	+ 1·0	92·0	90·49	8·0	9·41
6	1·05	+ 4·0	95·0	94·1	5·1	5·9
7	1·021	+ 6 1	97·9	96·48	2·1	3·52
8	1·01	+ 7 2	99·0	97·77	1·0	2·23
9	1·00	+ 9 0	100·0	99·88	0 0	0·12

The results have been plotted graphically (Fig. 4.). In Table II the calculated results showing the relationship existing between the percentage and the corresponding optical rotations have also been tabulated ; Landolt's law of mixture being applied for these calculations. The law states that if P_1 parts of a liquid of specific rotation $[\alpha_1]_D$ be mixed with P_2 parts of another liquid of $[\alpha_2]_D$ and if the specific rotation of the mixture be $[\alpha_m]_D$, then

$$[\alpha_m]_D = \frac{P_1[\alpha_1]_D + P_2[\alpha_2]_D}{P_1 + P_2}.$$

In this investigation only pure samples of oil (without any solvent) were used in the polarimetric tube. It has actually been determined that rotation of pure α-santalol

is $\alpha_{5780} = +9{\cdot}02$, and that of β-santalol $\alpha_{5780} = -76{\cdot}10$ Therefore, applying these

FIG. 3.

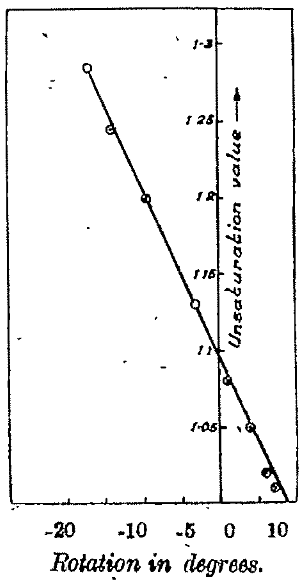


FIG. 4.

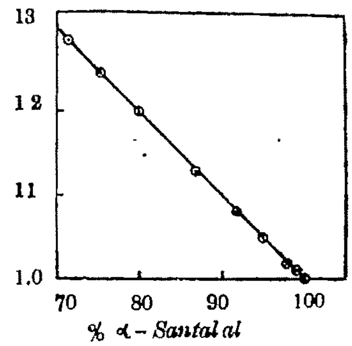
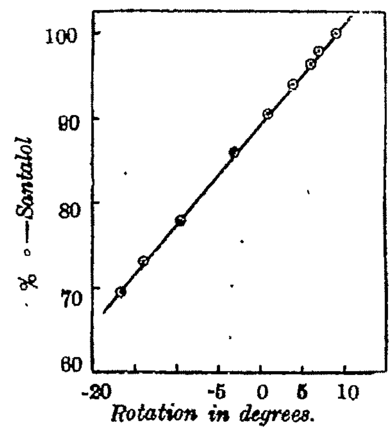


FIG. 5.



data in the above equation an approximare composition of a mixture can be easily calculated. These results have also been plotted graphically (Fig. 5).

Comparison of the Unsaturation-percentage and the Percentage—rotation Graphs.

For determining the composition of a santalol-mixture the unsaturation-percentage graph is more reliable. The composition, as determined from the percentage-rotation graph may not be entirely accurate due to two reasons : *viz.* (*i*) during the long course of distillation differential racemisation of the two santalols may take place ; (*ii*) Landolt's law of mixture may not be accurate in case of substances containing hydroxyl groups, which have been shown by different workers to have a tendency towards association and inter-influence (Ramsay and Shields, *Z. physikal. Chem.*, 1893, **12**, 431). The difference in the densities of the two santalols will also slightly affect the results. It is worth mentioning in this connection that inspite of the facts cited above, the results are found to be fairly accurate. It appears from Table II that a slight difference really exists between the results of composition as calculated from the unsaturation numbers and the corresponding optical rotations, the difference decreasing with the decreasing percentage of β-santalol It is not improbable that the presence of the α- and β-variety together may have some slight inter-influence on the rotations of each other.

The unsaturation-percentage graph is of course free from these anomalies, the unsaturation number of a substance being very little affected under ordinary circumstances. From a study of these graphs it is now possible to determine the purity of

α-santalol samples isolated by earlier workers. Semmler's sample, having an optical rotation of $+1°$, thus contained near about 10 % β-santalol as impurity.

Properties of α-Santalol.—B.p. 148°/5 mm ; 145°/4 mm. ; $\alpha_{5780} = +9{\cdot}02°$; $\alpha_{5460} = +10{\cdot}4°$; $n_D^{25} = 1{\cdot}5016$; $d_{25}^{25} = 0{\cdot}977$; $[R_L]_D = 66{\cdot}4$. Calc. $C_{15}H_{24}O\sqrt{1}$ 65 93. Exaltation is in conformity with the existence of a *cyclo*propane ring. Strychnine salt of hydrogen phthalate, m.p. 146°.

Isolation of β-Santalol.

Fraction B_2 was repeatedly fractionated through column No. 1 and the portion coming at 156-158°/5 mm. was collected. The unsaturation number and the corresponding polarimetric readings have been tabulated below (Table III). The optical rotation $\alpha_{5780} = -61{\cdot}6°$, and the corresponding unsaturation number "1·843" became constant after 19 distillations corresponding to 84·3% β-santalol. Pure β-santalol was then prepared from it by the application of chemical operations (Simonsen, *loc. cit.*, Paolini and Divizia, *loc. cit.*) as stated (*vide infra*).

TABLE III

No. of distillation.	Rotation in degrees α_{5780}	Unsaturation number.	No. of distillation.	Rotation in degrees α_{5780}	Unsaturation number.
1	−26·0	1·423	11	−53·68	...
2	−30·1	...	12	−55·0	1·761
3	−34·0	1·524	13	−56·3	
4	−38·21	...	14	−57·41	...
5	−41·3	1·614	15	−58·3	1.805
6	−44·22	...	16	−59·0	...
7	−47·1	1 68	17	−59·7	...
8	−49·25	...	18	−60 6	...
9	−50·95	1·72	19	−61·6	1·843
10	−52·31	...			

The above results have been plotted graphically (Fig. 6) and the graph extended to a point indicating the unsaturation number "2", which is the value for that of pure β-santalol. The optical rotation corresponding to this point should be the rotation of pure β-santalol. In fact the value (−75°) thus obtained tallies farely well with the value $\alpha_{5780} = -76{\cdot}1°$ actually determined.

Isolation of pure β-Santalol.—The impure β-santalol, obtained as above, was converted into acid phthalate in the usual way and this was then converted into the strychnine salt by boiling in alcoholic solution with the requisite amount of strychnine. The salt on fractional crystallisation and subsequent hydrolysis and

distillation furnished pure β-santalol having an unsaturation number "2" and α_{5780} = —76·1°.

As in the case of α-santalol, the relationship existing between the percentage proportion and unsaturation value has been shown in Table IV, and the results

FIG. 6.

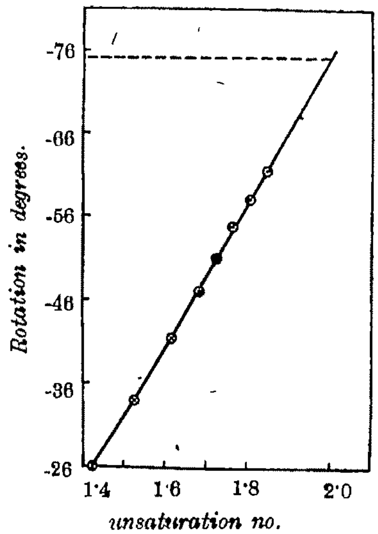


FIG. 7.

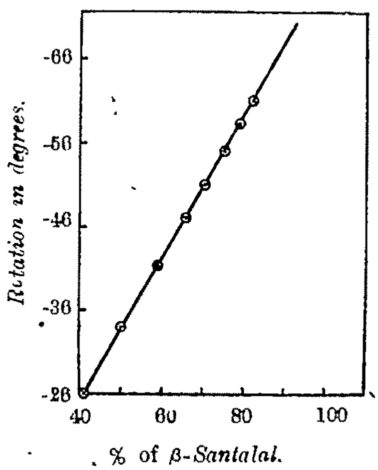
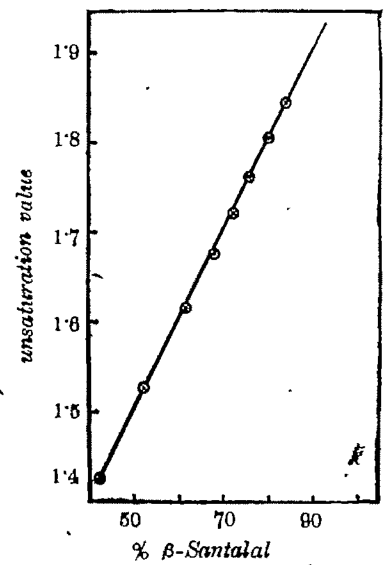


FIG. 8.



plotted graphically in Fig. 7. Similarly, the results of percentage-proportion and the corresponding optical rotations have also been arranged in the same table. The results have also been plotted in Fig. 8.

TABLE IV.

No	Unsaturation number.	α_{6780} in degrees	Percentage of β-Santalol from unsaturation.	Percentage of β-Santalol from rotation.	Percentage of α-santalol from unsaturation.	Percentage of α-santalol from rotation.
1	1·425	−26·0	42.5	41·08	57·5	58·92
2	1·524	−34·0	52·4	50·59	47·6	49·41
3	1·614	−41·3	61·4	59·16	38·6	40·84
4	1·68	−47·1	68·0	65·96	32·0	34·04
5	1·72	−50 95	72·0	70·48	28·0	29·52
6	1 761	−55·0	76·1	75·24	23·9	24·76
7	1·805	−58·3	80·5	79 12	19·5	20·88
8	1·843	−61·1	83·3	82·4	16·7	17·6

The arguments offered to explain the discrepancies in the composition as determined from the unsaturation value and optical rotations in the case of α-santalol are equally applicable in this case also.

Properties of β-Santalol.—B.p. 157°/5 mm., 15°/3 mm. d_{25}^{25}, 0·9719 ; n_{D}^{25}, 1·5102 ; $[R_L]_D$ = 67·7 ; Calc. $C_{15}H_{24}O$ $\sqrt{2}$ = 67·66 ; α_{5780} = −76·1° ; α_{5460} = −87·4°.

Isolation of α-Santalene

Fraction A_1 was subjected to three preliminary fractional distillations and the fraction boiling at 113-118°/5 mm. was treated in the usual way successively with saturated bisulphite solution and with phthalic anhydride to remove the aldehydic and ketonic as also the alcoholic impurities. The treated oil was then distilled over sodium and the distillate, thus obtained, was fractionated repeatedly through the column No. 2 and the portion coming at 113-115°/5 mm. was collected. Optical rotations and unsaturation numbers were noted as previously.

TABLE V

No. of distillation.	Rotation in degrees α_{5780}	Unsaturation number.	Percentage of α-santalene from unsaturation.	Percentage of β-santalene
12	−0.91	1,177	88.3	11.7
16	+2 6	1,07	...	...
17	+2.06	1.07	93.0	7.0

From the above results, the probable optical rotations of pure α-and β-santalene have been determined by calcularion, as follows, the percentage-proportion as determined from the unsaturation value having been taken to be correctly applicable in the case of the determination of percentage-proportion from optical rotation as well.

When there is 88·3 % α-santalene and 11·7 % β-santalene

$$\alpha_{5780} = -0·91,$$

and when there is 9·3 % α-santalene and 7 % β-santalene

$$\alpha_{5780} = +2·06.$$

Therefore, if X be the optical rotation of pure α-santalene and Y that of pure β-santalene then

$$\frac{93X+7Y}{93+7} = +2·06 \text{ and } \frac{88·3X+11·7Y}{88·3+11·7} = -0·91$$

Solving X (probable α_{5780} of pure α-santalene) = +6·48°

Y (probable α_{5780} of pure β-santalene) = −56·6°

The results may also be obtained graphically. Among the earlier workers, the purest sample of α-santalene isolated by Schimmel & Co. (*loc. cit.*) had an optical rotation α_D = −3°.

As the amount of material at our disposal was rather limited and also because the santalenes are present in the oil to the extent of only about 4-6 % it has not been possible to study them as exhaustively as in the case of the santalols. Moreover, the tendency of the hydrocarbons to accompany each other during

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fractionations is far more well pronounced than in the case of the alcohols. Besides there being no chemical process of purification available for the isolation of the hydrocarbons, the figures attributed to the optical rotations of the α- and β-santalenes may not be entirely correct.

Properties of author's Sample of α-Santalene.—B.p. 117°/7 mm.; $\alpha_{5780} = +2{\cdot}06$; $d_4^{20} = 0{\cdot}9102$; $n_D^{20} = 1{\cdot}4900$; $[R_L]_D = 64{\cdot}91$; $C_{15}H_{24}\sqrt{1} = 64{\cdot}4$. Exaltation is in conformity with the existence of *cyclo*propane ring. Probable optical rotation of pure variety $\alpha_{5780} = +6{\cdot}48°$. This result is of course open to slight variation.

Isolation of pure β-Santalene

Fraction A_2 was subjected to three preliminary fractions and the portion coming at 121-25°/5 mm. was purified from impurities as in the case of α-santalene and then fractionated repeatedly through column No 2 at 123-24°/5 mm. When the optical rotation (α_{5780}) and the corresponding unsaturation number came to $-49{\cdot}9°$ and 1·88 respectively, no further purification was possible. This corresponded to 88 % β-santalene.

Properties.—B.p. 125°/7 mm.; $\alpha_{5780} = -49{\cdot}9°$; $n_D^{20} = 1{\cdot}4941$; $d_4^{20} = 0{\cdot}8940$; $[R_L]_D = 66{\cdot}4$; Calc. for $C_{15}H_{24}\sqrt{2} = 66{\cdot}136$. Probable optical rotation of pure variety $\alpha_{5780} = -56{\cdot}6°$. This result is also open to slight variation.

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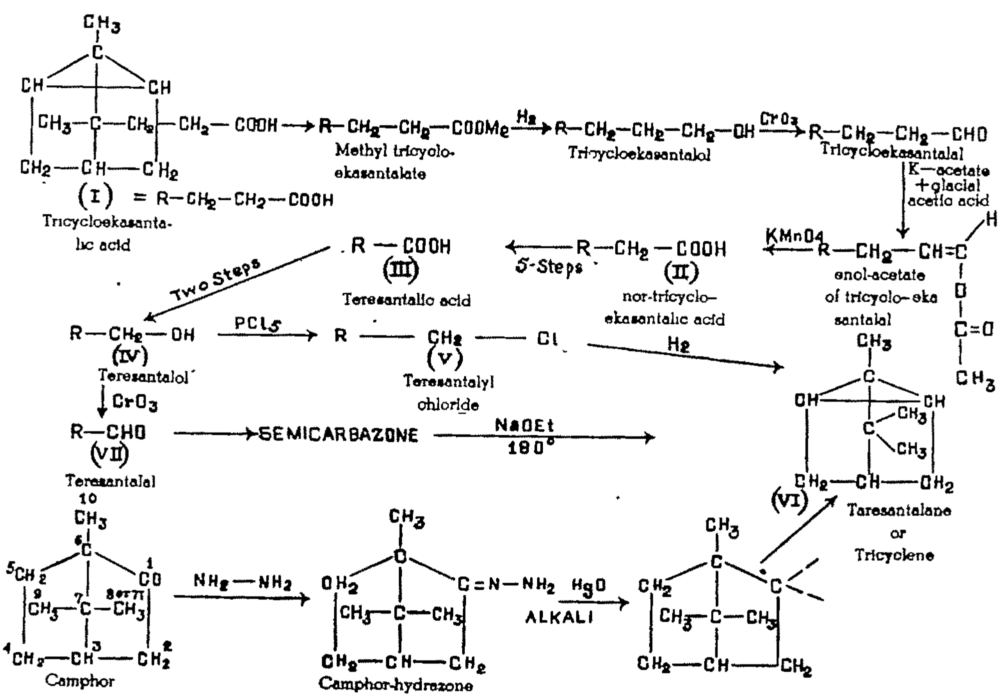
STUDIES IN THE SANTALOL SERIES. PART II. SYNTHESES OF *d*-AND *dl*-π-HYDROXYCAMPHOR, *d*-AND *dl*-TERESANTALOL AND *d*-AND *dl*-TRI*CYCLO* EKASANTALIC ACID

By P. C. Guha and S. C. Bhattacharyya

Starting from camphor and passing through a series of synthetic operations, it has been possible to synthesise *d*-and *dl*-π-hydroxycamphor, *d*-and *dl*-teresantalol and *d*-and *dl*-tri*cyclo*ekasantalic acid.

From part I of this series it is evident that the main constituent of East Indian sandalwood oil is the alcohol, α-santalol. The structure of this compound has been definitely established through the researches of Semmler (*Ber.*, 1910, **43**, 1893), Ruzicka (*Helv. Chim. Acta*, 1925, **9**, 140) and Simonsen (*J. Chem. Soc.*, 1935, 309). On oxidation with potassium permanganate α-santalol is converted into tri*cyclo*ekasantalic acid ($C_{12}H_{18}O_2$) (Semmler, *Ber.*, 1907, **40**, 1120; Chapmann and Burgess, *Proc. Chem. Soc.*, 1896, **12**, 140; *J. Chem. Soc.*, 1901, **79**, 134). Semmler ascribed the structure (I) to tri*cyclo*ekasantalic acid from the products of degradation of (I) successively to nor-tri*cyclo*ekasantalic acid (II) (*Ber.*, 1909, **42**, 584; 1910, **43**, 1723), teresantalic acid (III), teresantalol (IV) (*Ber.*, 1907, **40**, 3321, 3107), teresantalyl chloride (V) and teresantalane (VI).



If Semmler's formula for tri*cyclo*ekasantalic acid (I) is correct, teresantalene (VI) should be identical with tricyclene (Meerwein and Emster, *Ber.*, 1920, **53**, 1815).

This identity of teresantalene with tricyclene has been established by Ruzicka and Liebel (*loc. cit.*) by converting (IV) into the corresponding aldehyde, teresantalal (VII), the semicarbazone of which on treatment with sodium ethylate gave tricyclene. The synthesis of the hydrocarbon tricyclene by oxidising camphor-hydrazone with mercuric oxide in alkaline solution (Meerwein and Emster, *loc. cit.*) leaves no doubt about the correctness of the structure (VI). It is therefore evident that tri*cyclo*ekasantalic acid (I) and its degradation products are derivatives of tricyclene (VI) and as such are related to π-derivatives of camphor (*vide* formula). It appeared to us feasible to synthesise tri*cyclo*ekasantalic acid (I) and its products of degradation from suitable π-derivatives of camphor. (*cf.* however, Asahina, *Ber.*, 1934, **67**, 76 ; 1935, **68**, 952 ; Sahasi and Iki, *Sci. papars Inst. Phys. Chem. Res. Japan*, 1934, **25**, 48, 73).

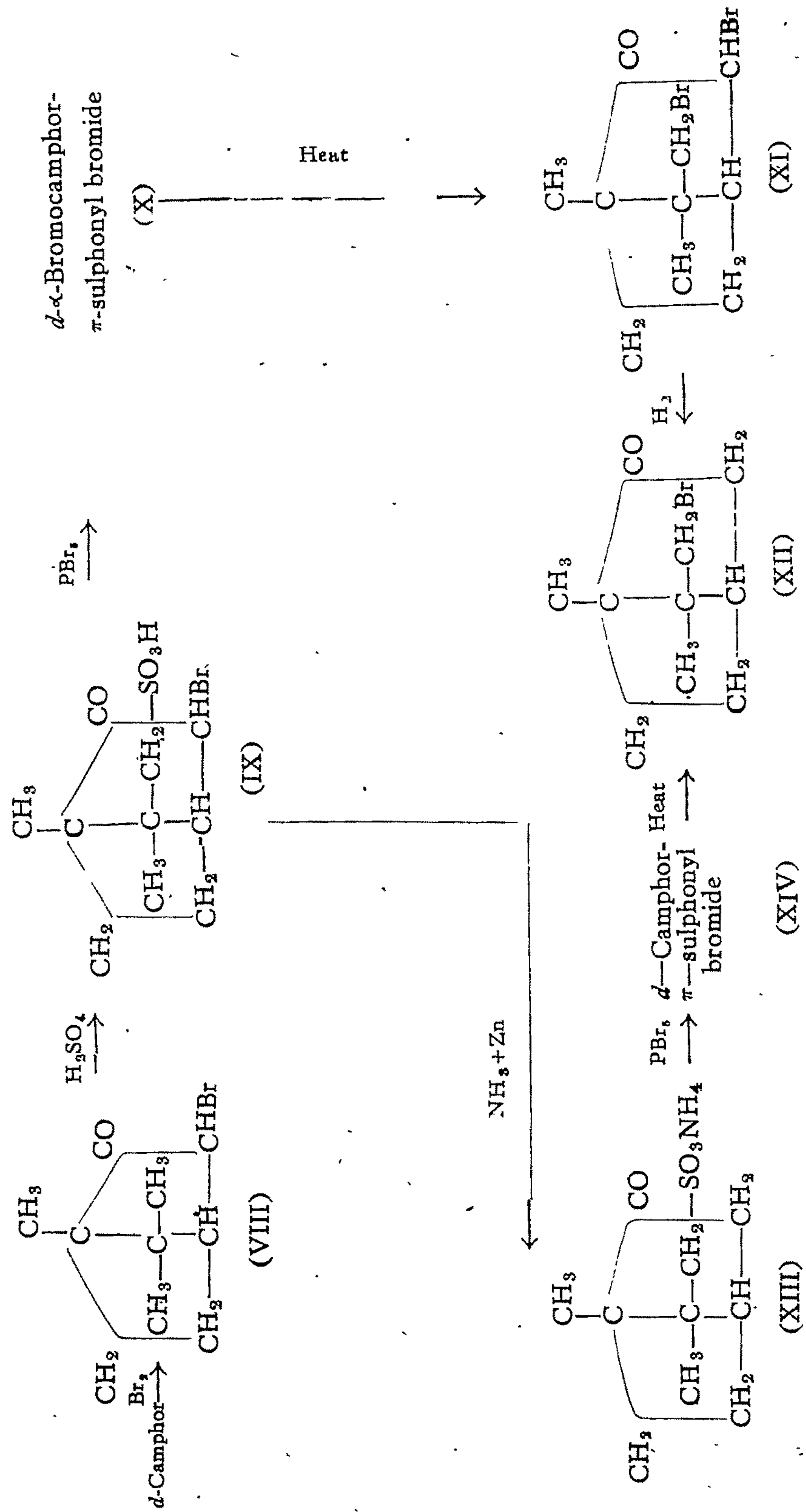
Taking camphor as our starting material, it has been possible to synthesise (I) by passing through the syntheses of π-hydroxycamphor, teresantalol (IV) and teresantalyl chloride (V). *d*-π-Bromocamphor, which was the essential material for this investigation, was prepared from camphor according to the method of Pope and Kipping (*J. Chem. Soc.*, 1893, **63**, 553 ; 1895, **65**, 357) with some modifications.

d-Camphor was brominated to *d*-α-bromocamphor (VIII), which on sulphonation either with fuming sulphuric acid or chlorosulphonic acid, furnished the corresponding π-sulphonic acid (IX). The ammonium salt of (IX) was converted by phosphorus pentabromide into the corresponding sulphonyl bromide (X) which on being heated above its melting point was converted almost quantitatively into *d*-$\alpha\pi$-dibromocamphor (XI) with the elimination of sulphur dioxide. Dibromocamphor (XI) on reduction with zinc and acetic acid was converted in to *d*-π-bromocamphor (XII) ; only the α-bromine atom being replaced by hydrogen The compound (XII) was also prepared by first reducing the ammonium salt of (IX) with zinc dust and ammonia to the ammonium salt of *d*-camphor-π-sulphonic acid (XIII). This in its turn was converted into the corresponding sulphonyl bromide (XV) which on heating above its melting point furnished (XII). (See page. 273).

Both the methods for the preparation of compound (XII) were found to be equally satisfactory but in the former process a little caution was necessary during the reduction of (XI), as otherwise the reaction is attended with the formation of some non-halogenated products.

Unsubstituted *d*-and *dl*-camphor on sulphonation produced inactive camphor-π-sulphonic acid, the active camphor being racemised during sulphonation. This inctive sulphonic acid was converted into *dl*-π-bromocamphor exactly according to the process mentioned previously. It has, however, been observed that the yield of reaction products obtained with the inactive compounds gets always very much diminished in quantity. Equally unsatisfactory results were obtained when chlorine was used in place of bromine and phosphorus pentachloride in place of pentabromide.

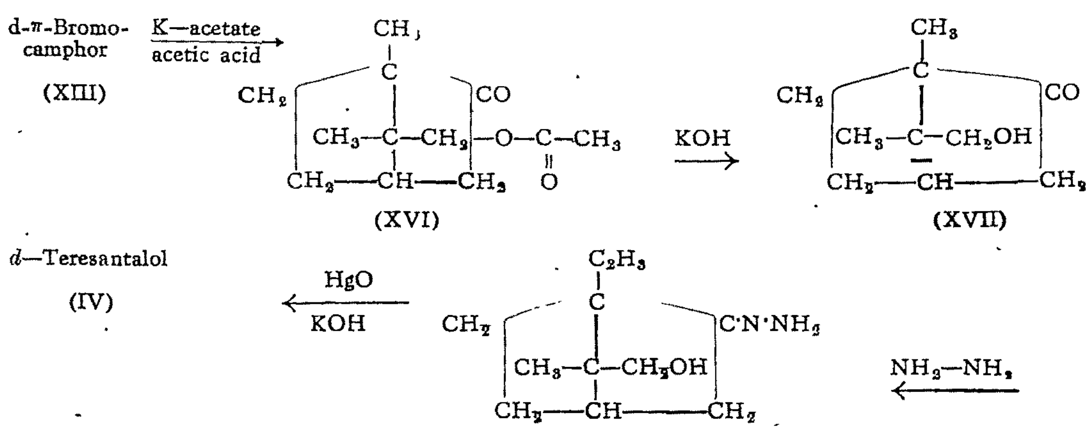
The bromine atom of *d*-π-bromo-camphor (XII), as is evident from its method eparation by the reduction of (XI), is comparatively inert. It cannot be


d-Camphor
Br₂
H₂SO₄
(VIII)
(IX)
PBr₅
d-α-Bromocamphor-π-sulphonyl bromide (X)
Heat
(XI)
H₂
(XII)
NH₃+Zn
(XIII)
PBr₅
d—Camphor-π—sulphonyl bromide
(XIV)
Heat

hydrolysed even by 30% alcoholic alkali under pressure and it does not react with magnesium in ethyl or amyl ether to produce the corresponding Grignard compound. It does not react with potassium or sodium derivative of ethyl malonate. This peculiar inertness of the π-bromine atom does not seem to have been thoroughly examined by earlier workers. It is, however, well known (Kipping, *J. Chem. Soc.*, 1896, **69**, 913, 928) that when the π-bromocamphor is oxidised to bromocamphoric acid, the inertness of the bromine atom in the latter completely disappears. It is clear therefore that the inertness of the bromine atom in π-bromocamphor is due to the steric influence exerted by the bicyclic structure.

As it appears to be the easiest process, an attempt has been made to prepare teresantalyl bromide directly from (XII) by converting it into the corresponding hydrazone and subsequently oxidising the latter in the usual way with yellow oxide of mercury. But instead of the desired product, a mixture containing traces of a compound which from its melting point appears to be teresantalol, tricyclene and an azo compound are obtained. The following method has been adopted for the preparation of teresantalol and its derivatives.

The compound (XII) is boiled with potassium acetate and glacial acetic acid, and thus converted into an acetoxy derivative (XVI) which on hydrolysis furnishes *d*-π-hydroxycamphor (XVII). The hydrazone (XVIII) of this hydroxy-ketone (XVII) on oxidation with mercuric oxide in alkaline solution produces *d*-teresantalol (IV). The action of hydrazine hydrate (50%) in alcoholic solution on camphor and π-hydroxycamphor is very slow, about 170 hours being necessary for the completion of the reaction. The same reaction, however, is completed within 12 hours when camphor or π-hydroxycamphor is slowly refluxed with 100% hydrazine hydrate.



The hydroxyl group in teresantalol (IV) is also comparatively inert. On treatment with excess of thionyl chloride in pyridine solution it gives a poor yield of teresatnalyl chloride. Impure teresantalyl chloride has been prepared by the action of phosphorus pentachloride on teresantalol (IV) in low boiling petrol. It is a well known fact that *cyclo*propane ring is vulnerable to the action of phosphorus

pentahalides and in fact all reagents which produce hydrogen halides attack a *cyclo*-propane ring with the production of chlorinated bicyclic decomposition products. It is because of this reason that Semmler's teresantalane (VI) could not be identified with tricyclene. Teresantalyl chloride, which has been used for this purpose, is prepared by the action of phosphorus pentachloride on the corresponding alcohol teresantalol, during which operation some chlorinated bicyclic decomposition products are formed, which appear to have been responsible for Semmler's difficulty in identifying teresantalane with tricyclene.

Similar difficulties are encountered in the thujane series (Semmler, *Ber.*, 1892, **25**, 3345 ; Kondakov, *J. prakut. Chem.*, 1900, *ii*, **62**, 176) *viz.* in the preparation of thujyl chloride by the action of phosphorus pentachloride on thujyl alcohol, when besides the partial formation of thujyl chloride, there are also formed some impure products by the rupture of the *cyclo*propane ring.

The halogen atom in teresantalyl chloride (V) is inert and does not react with sodium derivative of malonic ester in either benzene or alcoholic solution. It is condensed with potassium derivative of ethyl malonate in xylene suspension under pressure with the formation of impure teresantalyl malonic ester (XIX). The free malonic acid derivative separates in an oily form and could not be crystallised, and eliminates carbon dioxide on heating. From the residual oil tri*cyclo*-ekasantalic acid (I) could be isolated by steam distillation. The yield is only about 3 % of the theoretical amount.

$$\underset{\text{(XIX)}}{R—CH_2—CH\begin{cases}COOEt\\COOEt\end{cases}} \xrightarrow{KOH} R—CH_2—CH\begin{cases}COOH\\COOH\end{cases} \xrightarrow{-CO_2} \underset{\text{(I)}}{R—CH_2—CH_2—COOH}$$

Tri*cyclo*ekasantalic acid, thus prepared, has a feeble *dextro*-rotation showing that partial racemisation has taken place during the course of reaction. The success of this experiment depends entirely on the successful preparation of teresantalyl chloride (V) in which operation the treatment with phosphorus pentachloride should not be allowed to be too drastic.

The corresponding inactive compounds of the series could be prepared in an exactly analogous manner from inactive π-bromocamphor.

EXPERIMENTAL

d-α-Bromocamphor was obtained by directly brominating *d*-camphor according to the method of Armstrong (*Chem. News*, 1878, **37**, 4) ; camphor (152 g.) gave α-bromocamphor (190-200 g.), m.p. 76° ; $[\alpha]_D = +140°$.

Sulphonation of α-bromo camphor was carried out according to the following three processes using

(*i*) chlorosulphonic acid in chloroform solution, (Pope and Kipping, *loc. cit.*),
(*ii*) chlorosulphonic acid but without any solvent,
(*iii*) fuming sulphuric acid of a particular concentration.

All the processes were found to be satisfactory, but the second one was the most convenient. In this process (*i*) almost 50% of chloroform used (about 133 c.c. for 100 g. of bromocamphor) is lost and sulphonation also takes about 12 hours for completion. In process (*iii*) a huge amount of calcium sulphate requires to be dealt with, whereas in method (*ii*) no such difficulties are encountered. The process is described below :

d-α-Bromocamphor (100 g.) was placed in a round-bottom flask fitted with a long condenser, a dropping funnel and calcium chloride guard tube. Chlorosulphonic acid (75 c.c.) was then added in three instalments at intervals of 5 minutes under shaking. The flask was then warmed to 60°-70° on a water-bath for about 30 minutes until a sample of the reaction mixture dissolved completely in water. The brownish viscous mass was neutralised by sufficient amount of calcium carbonate suspended in water. The precipitated calcium sulphate was filtered off and washed thoroughly with water. To the hot filtrate the requisite amount of ammonium carbonate was added and the precipitated calcium carbonate was filtered off and washed. The solution of the ammonium salt on evaporation and cooling deposited crystals of ammonium *d*-α-bromocamphor-π-sulphonate, which after filtration and washing with 95% alcohol, gave beautiful colourless crystals, yield 90-100 g.

Ammonium salt of d-*Camphor-π-sulphonic Acid.*—*d*-Ammonium α-bromocamphor-π-sulphonate (250 g.) was dissolved in 10% ammonia solution (1000 c.c.) and zinc dust (100 g.) added gradually during 20 minutes, there being a considerable rise of temperature in the beginning. The mixture was then heated on the water-bath for 40 minutes, and the residual zinc dust filtered off. The hot filtrate was saturated with hydrogen sulphide and the precipitated zinc sulphide removed by filtration The filtrate containing ammonium salt of *d*-camphor-π-sulphonic acid and ammonium bromide in equivalent proportion was evaporated nearly to dryness and allowed to cool. The crystals obtained were further purified by washing successively with alcohol and ether. The yield of the ammonium salt and ammonium bromide was 265 g.

d-α-*Bromocamphor-π-sulphonyl Bromide.*—Dry. ammonium *d*-α-bromocamphor-π-sulphonate (60 g.) was treated with phosphorus pentabromide (85 g.) in the usual way (Pope and Kipping, *loc. cit.*) and the crude sulphonyl bromide crystallised from ethyl acetate, yield 35 g.,. softens at 137° and melts completely at 145° ; $[\alpha]_D$ in chloroform solution, +144·9°.

d-α-π-Dibromocamphor.—*d*-α-Bromocamphor-π-sulphonyl bromide (100 g.), taken in a 500 c.c. beaker and covered with a clock glass, was heated in a metal-bath. Decomposition commenced at 150°, the temperature was gradually raised to 160-170°

and kept there for about 10 minutes during which the evolution of sulphur dioxide was complete. The molten mass after cooling was dissolved in hot acetic acid containing a little nitric acid from which on cooling *d*-α-π-dibromocamphor precipitated. The substance was recrystallised from alcohol, yield 77 g., m.p. 152° ; $[\alpha]_D$, +98·99° (in chloroform solution).

d-π-*Bromocamphor.*—*d*-α-π-Dibromocamphor (47 g.) was dissolved in sufficient amount of 80% hot acetic acid and zinc dust (20 g.) was added during 10 minutes, care being taken that the reaction was neither too vigorous nor too sluggish. After the reaction subsided, the solution was filtered while hot and the residue on filter paper washed with hot acetic acid. The filtrate was cooled, diluted with a sufficient amount of cold water and allowed to stand overnight. The precipitated *d*-π-bromocamphor was filtered off, dried and crystallised from low boiling petrol, yield 34 g., m.p. 94° ; $[\alpha]_D$, 121·3° (in chloroform solution).

d-*Camphor*-π-*sulphonyl Bromide.*—Ammonium *d*-camphor-π-sulphonate (60 g.) was treated with phosphorus pentabromide in the usual way (Pope and Kipping, *loc. cit.*), the crude sulphonyl bromide was crystallised from ethyl acetate, yield 60-70%, m.p. 145° ; $[\alpha]_D$, +147·2°.

Decomposition of d-*camphor*-π-*sulphonyl Bromide to* d-π-*Bromocamphor.*—*d*-Camphor-sulphonyl bromide (100 g.) was decomposed exactly as in the case of *d*-α-bromocamphor-π-sulphonyl bromide but at a temperature of 150-160°. *d*-π-Bromocamphor crystallised from petrol-ether, yield 75 g., m.p. 94° ; $[\alpha]_D$, +121·9°.

Two methods of preparing *d*-π-bromocamphor have been described above : (*i*) by the reduction of *d*-α-π-dibromocamphor, (*ii*) by the decomposition of *d*-π-sulphonyl bromide.

Both the methods are equally satisfactory. But in method (*i*) some careful control of the reduction is necessary, otherwise some non-halogenated products are formed. Of course, if carefully performed, it gives a very satisfactory yield of *d*-π-bromocamphor. The method (*ii*) is free from all uncertain factors and is the surer of the above two methods.

dl-π-*Bromocamphor* was obtained in an analogous manner from *dl*-π-sulphonic acid which was obtained by the direct sulphonation of unsubstituted camphor with chlorosulphonic acid. The impure ammonium salt which could not be crystallised gave a 25% yield of *dl*-π-sulphonyl bromide (m p. 125-30°), which on subsequent decomposition above its melting point gave a nearly theoretical yield of *dl*-π-bromocamphor, m.p. 93·5°.

d-π-*Acetoxycamphor.*—*d*-π-Bromocamphor (50 g.), anhydrous potassium acetate (100 g.), and glacial acetic acid (100 g.) were slowly refluxed in an oil-bath (170-180°) for 24 hours. The product was poured into cold water, neutralised with soda and extracted with ether. The dry ethereal solution on evaporation and subsequent

distillation in vacuum gave *d-π*-acetoxycamphor, b.p. 123°/5 mm., yield 38·3 g. (Found : C, 67·1 ; H, 8·81. $C_{12}H_{18}O_3$ requires C, 68·57 ; H, 8·6 per cent).

The semicarbazone was prepared in the usual manner and crystallised from alcohol, m.p. 234°. (Found : C, 57·90 ; H, 7·72 ; N, 16·01. $C_{13}H_{21}O_3N_3$ requires C, 58·42 ; H, 7·90 ; N, 15·73 per cent).

d-*π-Hydroxycamphor.*—Acetoxycamphor (38·3 g.) was dissolved in 10% alcoholic potash solution (400 c.c.) and boiled for ½ hour. After distilling off the excess of alcohol, the residue was poured into cold water, saturated with common salt and extracted with ether. The residue left after distillation of ether was crystallised from a mixture of petrol and benzene ; yield 29·1 g., m. p. 234° ; $[\alpha]_D$, 63·6. (Found : C, 71·7 ; H, 9·82. $C_{10}H_{16}O_2$ requires C, 71·47 ; H, 9·52 per cent).

dl-*π-Hydroxycamphor* was prepared in an exactly analogous way from *dl-π*-bromocamphor, which was at first converted into the acetoxy derivative (b.p. 123°/4 mm.) and then by hydrolysis to *dl-π*-hydroxycamphor ; yield same as in the previous case, m.p. 233°. (Found : C, 71·29. H, 9·92. $C_{10}H_{16}O_2$ requires C, 71·47 ; H, 9·59 per cent).

It may be interesting to note that both *d*-and *dl-π*-hydroxycamphor did not form any semicarbazone in the usual way, but they gave hydrazones on treatment with hydrazine hydrate.

d-*Teresantalol.*—*d-π*-Hydroxycamphor (27 g.), and 100% hydrazine hydrate (10 g.) were dissolved in 50 c.c. of absolute alcohol and refluxed in a three-necked flask for 150-170 hours and thus converted into the hydrazone, (the same reaction may also be successfully performed by refluxing slowly a mixture of the hydroxy ketone, with 100% hydrate for 10-15 hours), which without being isolated was utilised for the subsequent reaction. To this mixture potassium hydroxide (4 g.), dissolved in 10 c.c. of water, and diluted with 50 c.c. of alcohol, was added and the mixture stirred mechanically. Freshly prepared yellow oxide of mercury (50 g.) was then gradually added during 10 minutes, brisk evolution of nitrogen taking place throughout the course of addition. Stirring was continued for another 24 hours, after which the mercuric slime was filtered off. The residual oil left after removal of alcohol was distilled in vacuum ; teresantalol distilled at about 90°/5 mm. and solidified inside the condenser. It was recrystallised from a mixture of petrol-ether and benzene, yield 13 g., m.p. 115° ; $[\alpha]_D$, +12·1° ; natural variety, m.p. 114° ; $[\alpha]_D$, 11·58. (Found : C, 79·1 ; H, 10·68. $C_{10}H_{16}O$ requires C, 78·9 ; H, 10·4 per cent).

Teresantalol is extremely volatile and great care should be taken during its distillation.

dl-*Teresantalol* was prepared in an analogous way from *dl-π*-hydroxycamphor, m.p. 117°. (Found : C, 79·0 ; H, 10·71. $C_{10}H_{16}O$ requires C, 78·7 ; H, 10·6 per cent).

d-*Teresantalyl Chloride.*—*d*-Teresantalol (30 g.) was covered with a few c.c. of petrol-ether and phosphorus pentachloride (1¼ mol.) was added gradually. The

mixture was triturated for about 20 minutes and left aside for 5-10 minutes and then poured into ice-water, extracted with ether, washed with cold water and distilled in vacuum. Teresantalyl chloride distilled at 77-87°/9 mm. The substance emitted an acrid smell.

d-*Teresantalylmalonic Ester*.—Clean potassium (7·8 g.; 2 mol.) was dissolved in absolute alcohol (200 c. c.) contained in a three-necked flask fitted with a reflux condenser and a guard tube. Malonic ester (32 g.) was then added and the mixture heated on the water-bath for ½ hour. Alcohol was then completely removed at 120-140° under reduced pressure and sodium-dried xylene (180 c. c.) containing teresantlayl chloride (17·1g.) was poured in. The mixture was transferred to a soda-water bottle and heated under pressure at 170-190° for 30 hours. From the filtered solution xylene was removed by distillation under diminished pressure and the residue was distilled under vacuum. Teresantalylmalonic ester came over at 130-145°/13 mm., yield 8 g.

As envisaged by subsequent investigation, only a minor portion of the distillate was teresantalylmalonic ester, the rest being other impurities.

Teresantalyl chloride, used by us, was impure and contained some acidic impurities; when the above reaction was done in alcoholic solution under ordinary pressure nearly one atomic proportion of sodium or potassium was neutralised and alkali halides separated easily. From the reaction mixture free malonic ester could be detected, but no teresantalylmalonic ester was formed. Similar results were obtained in benzene suspension, Expected result could only be obtained in xylene suspension under pressure and using an excess of potassium. Teresantalyl chloride used in this reaction should be freshly prepared.

d-*Tricycloekasantalic Acid*.—Impure teresantalyl malonic ester, as obtained above, was hydrolysed with alcoholic potash (10%) and then just acidified with dilute sulphuric acid and extracted with ether. From the ethereal extract, teresantalylmalonic acid could not be crystallised. The impure oily liquid was heated in an oil-bath at 180-200°, when carbon dioxide began to evolve. After the evolution of carbon dioxide had ceased, the viscous mass was subjected to steam distillation. *d*-Tri*cyclo*ekasantalic acid came over with steam as a semi-solid mass and was recrystallised from alcohol and then from low boiling petrol; yield 0·9g. (3-4% of theory); m. p. 76°; $[\alpha]_{5780}$, +1·0 to +3·1°; variety from natural source, m.p. 76·4°; $[\alpha]_{5780}$, +15·4°.

Equivalent weight was determined by titration in alcoholic solution with standard alkali using phenolphthalein as indicator (Found: C, 74·61; H, 9·30. Equiv. 191·1. $C_{12}H_{18}O_2$ requires C, 74·19; H, 9·33 per cent. Equiv. 192·25).

The Methyl ester was prepared from the silver salt and alkyl iodide, b.p. 127°/10 mm.; d^{20}_{4}, 1·0165; n^{20}_{D}, 1·4782. (Found: C, 74·71; H, 9·61. $C_{13}H_{20}O_2$ requires C, 74·95; H, 9·3 per cent).

dl-*Tricycloekasantalic acid* was prepared in an analogous way. Crystallisation in this case was comparatively difficult and the yield was even poorer; m.p. 75°: Equiv. wt. 194·2. (Found: C, 73·99; H, 9.60. $C_{12}H_{18}O_2$ requires C, 74·19; H, 9·33 per cent). Methyl ester, b. p. 127°/10 mm; n^{20}_{D}, 1·4783 (Found: C, 74·3; H, 10·1. $C_{13}H_{22}O_2$ requires C, 74·3; H, 10·5 per cent).

Further work for the preparation of optically pure tri*cyclo*ekasantalic acid by a different method is in progress.

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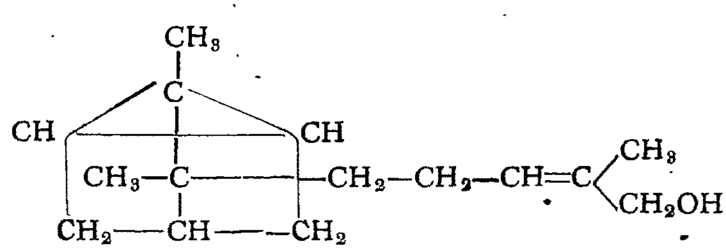
Received June 2, 1944

STUDIES IN THE SANTALOL SERIES. PART III. SYNTHESES OF *d*-α-SANTALAL AND *d*-α-SANTALOL

By P. C. Guha and S. C. Bhattacharyya

The aldehyde tri*cyclo*ekasantalal has been condensed with propionic aldehyde in presence of alcoholic alkali to produce *d*-santalal. Santalal has been reduced with aluminium ethoxide to *d*-α-santalol, identical with the natural product.

In Part II of this series, the syntheses of some of the degradation products of *d*-α-santalol has been dealt with. In this part, the syntheses of the parent substance *d*-α-santalol, as also of the corresponding aldehyde *d*-α-santalal has been described. Semmler made a very exhaustive study of the chemistry of the degradation products of α-santalol and ascribed to it ($C_{15}H_{24}O$) the structure (I).



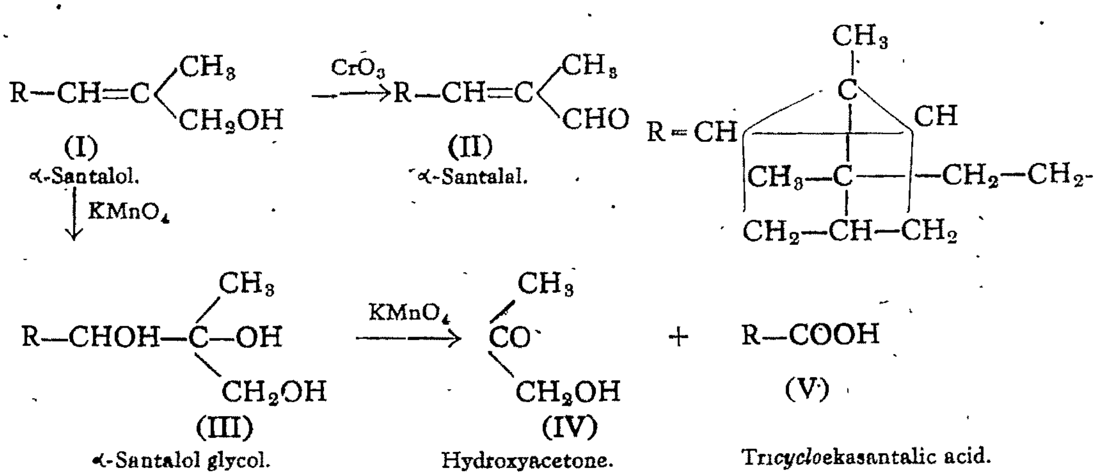
(I)

α-Santalol.

According to him, α-santalol (I) is a tricyclic primary alcohol with a long side-chain possessing an ethylenic linkage. When *d*-α-santalol (I) is oxidised with chromic

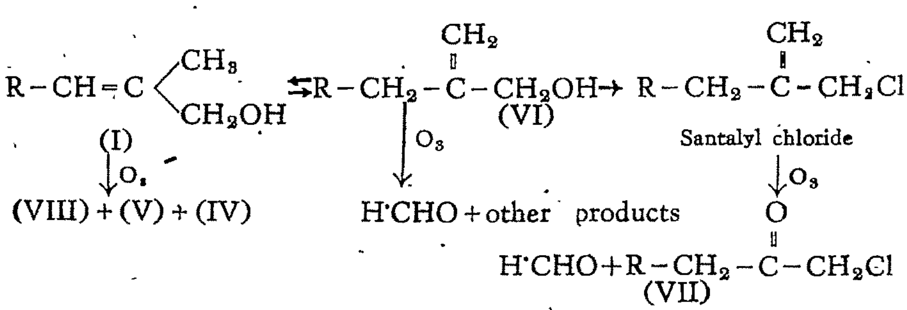
acid in acetic acid solution (Semmler, *Ber.*, 1907, **40**, 1120, 1124) it forms the aldehyde *d*-α-santalal, $C_{15}H_{22}O$ (II). With dilute permanganate solution α-santalol (I) produces α-santalol glycol (III) which is subsequently oxidised to hydroxyacetone (IV) and tri*cyclo*ekasantalic acid (V) (Semmler, *loc. cit.*, Simonsen, *J. Chem. Soc.*, 1935, 309).

Structure of tri*cyclo*ekasantalic acid was known from the work of Semmler (*Ber.*, 1910, 43, 445, 1723, 1893) and has been definitely established from our synthesis described in Part II of this series. Therefore, α-santalol must have the structure (I), consequently α-santalal must be represented by (II).



Tautomerism.—Recently Simonsen (*loc. cit.*) has made the important observation that α-santalol (I) exists in a tautomeric form (VI).

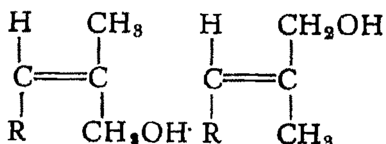
Simonsen, besides isolating tri*cyclo*ekasantalic acid, tri*cyclo*ekasantalal (VIII) (Semmler, *Ber.*, 1907, 40, 1120) and hydroxyacetone (IV) from the products of ozonolysis of α-santalol (I), has also established the presence of formaldehyde by preparing its characteristic methone derivative. Moreover, by the ozonolysis of α-santalyl chloride he could isolate, though in an impure form, a chloroketone (VII) and formaldehyde. The results can only be interpreted on the assumption that α-santalol (I) can exist in a second tautomeric form (VI).



Here is a peculiar difficulty in interpreting oxidation experiments where the groups $\mathrm{C{-}C}\Big\langle{{=}\mathrm{C} \atop \mathrm{C}}$ and $\mathrm{C{-}C}\Big\langle{\mathrm{C} \atop \mathrm{C}}$ are involved, since products corresponding to both the forms are obtained. These phenomena, though they appear rather peculiar, are not quite uncommon among the terpenes.

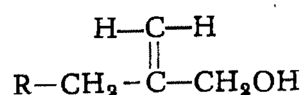
Kuhn and Roth (*Ber.*, 1932, **65**, 1255) quantitatively estimated the amount of acetone formed during the oxidation of similar compounds (e.g. dehydrogeranic acid) by ozone followed by potassium permanganate. They found that in general the quantity of acetone amounts to 60-90% of the theory, the quantity being still less with potassium permanganate-oxidation. This type of linkage is considered to be mobile either under the influence of reagents or in solution, and may be interpreted as due to tautomerism. According to Simonsen, santalol is endowed with this kind of tautomeric properties.

Some Stereochemical Considerations.—No mention seems to have been made by the earlier workers of the possibility of α-santalol molecule existing in three geometrically isomeric forms shown below :



(A) (B)

From Formula (I)



(C)

From Formula (VI)

On oxidation of α-santalol with ozone and permanganate, tri*cyclo*ekasantalic acid (V) and the corresponding aldehyde tri*cyclo*ekasantalal (VIII) are obtained as the main products. Consequently, it may be reasonably assumed that the major bulk of natural α-santalol consists of compound (I). Moreover, in the isolated variety of natural α-santalol, which had to undergo a long course of heating during isolation by repeated fractional distillation, it is probable that only the more stable variety of the forms (A) and (B) will predominate.

In Part II of this series, the synthesis of tri*cyclo*ekasantalic acid (V) has been described. In the experiments described in the present paper the corresponding aldehyde, tri*cyclo*ekasantalal (VIII) has been utilised as the starting material for building up the α-santalol molecule. Semmler (*loc. cit.*) has shown that the methyl ester of tri*cyclo*eksantalic acid gives the corresponding alcohol, tri*cyclo*ekasantalol (IX) on reduction ; the latter can be converted by oxidation into the corresponding aldehyde, tri*cyclo*ekasantalal (VIII).

$$\underset{(\mathrm{V})}{\mathrm{R{-}COOH}} \longrightarrow \mathrm{R{-}COCH_3} \xrightarrow{H_2} \underset{(\mathrm{IX})}{\mathrm{R{-}CH_2{-}OH}} \xrightarrow{CrO_3} \underset{(\mathrm{VIII})}{\mathrm{R{-}CHO}}$$

$$\underset{\alpha\text{-Santalol}}{} \xrightarrow{O_3} (\mathrm{VIII})$$

The same aldehyde can be obtained by the direct ozonolysis of natural α-santalol. The latter process of the ozonolysis of natural α-santalol has now been utilised for the preparation of this aldehyde. Because the synthesis of tri*cyclo*ekasantalic acid has now been achieved, that of the aldehyde follows automatically. It is therefore immaterial whichever process is utilised for the preparation of this aldehyde.

Tri*cyclo*ekasantalal (VIII) undergoes aldol condensation with propionic aldehyde in presence of dilute alcoholic alkali producing the unsaturated aldehyde, α-santalal (II), identical with the product obtained from natural α-santalol by oxidation.

$$\underset{\text{(VIII)}}{R{-}CHO} \longrightarrow \underset{\text{(X)}}{R\ CHOH{-}CH\begin{matrix} \diagup CH_3 \\ \diagdown CHO \end{matrix}} \xrightarrow{H_2O} R-CH=C\begin{matrix} \diagup CH_3 \\ \diagdown CHO \end{matrix}$$

$$\text{(I)} \xleftarrow{\text{Alethyl ate}}$$

The aldol (X), formed at the intermediate stage, could not be isolated. The yield used to vary due to the simultaneous self-condensation of propionic aldehyde, the maximum yield obtained was however 20%. α-Santalal (II), thus obtained, has been reduced with aluminium alcoholate to the alcohol, α-santalol (I), identical with the natural product. To elucidate the tautomeric character of synthetic α-santalol it was subjected to the process of ozonisation in the products of which no formaldehyde could be detected. As the amount of substance at our disposal was very limited, the inference of the ozonisation experiment cannot be regarded as confirmed. Further experiments on the direct synthesis of the tautomeric variety (C) are in progress.

EXPERIMENTAL

*Tri*cyclo*ekasantalal.*—Pure natural α-santalol (20 g.) was ozonised in ethyl acetate solution. After the ozonisation was complete, the solvent was removed by distillation under reduced pressure and the ozonide of α-santalol decomposed by heating with water and shaken thoroughly with potassium bicarbonate solution to remove any tri*cyclo*ekasantalic acid formed. The insoluble oily layer after extraction with ether was distilled in vacuum. The aldehyde was then purified through its bisulphite compound in the usual way and finally redistilled. Yield was variable 3—3·5g. could be obtained ; b.p. 110°111°/10 mm ; n^{20}_D, 1·4852 ; d^{20}_4, 0·9845 ; α_D, +14·4° ; semicarbazone, m.p. 163°.

Synthesis of α-Santalal.—Pure tri*cyclo*ekasantalal (8·9 g.) and freshly distilled propionic aldehyde (3 g.) were dissolved in 1·5—3% alcoholic potash (150 c.c.) contained in a round-bottomed flask, connected with a tall reflux condenser and left for 5 days at the ordinary temperature. The mixture was slowly warmed on the water-bath for about a day. The residual oil left after distillation of alcohol was extracted with ether, washed, dried and fractionated in vacuum. At first a low boiling fraction came out which was the self-condensation product of propionic aldehyde, then a

small amount of a second fraction, b.p. 100°/5 mm. which was nothing but *tricyclo*-ekasantalal. The third fraction, b.p. 138-145°/5 mm., was α-santalal. A higher boiling residue remained in the flask. The third fraction was redistilled ; *d*-santalal distilled at 143°/5 mm. It was finally purified through its semicarbazone. Pure aldehyde was prepared from the semicarbazone by decomposing the latter with phthalic anhydride and distilling in steam according to the method of Semmler (*loc. cit.*), yield 2·2 g. (approx) ; b.p. 143°/5 mm. , 153°/10 mm. ; n^{20}_{D}, 1·5104 ; α_D, +14·1° ; d^{20}_{4}, 0·9951. (Found : C, 82·78 ; H, 10·81. Calc. for $C_{15}H_{22}O$: C, 82·5 ; H, 10·1 per cent.). (As it is an α β-unsaturated aldehyde, it is liable to undergo Cannizzaro's reaction and traces of a substance appearing like α-santalic acid (*vide* part IV) could be detected in the residue left in the flask.)

The semicarbazone was prepared in the usual way from santalal (1 g.), semicarbazide hydrochloride (1·2 g.), sodium acetate (1·5 g.) in alcoholic solution. The precipitate was recrystallised from alcohol ; m.p. 219-20° (corrected). Sample of santalal-semicarbazone, prepared from natural α-santalol, melts at 220°. (Found : C, 69·5 ; H, 9·36 ; N, 15·57. Calc. for $C_{16}H_{25}ON_3$: C, 69·81 ; H, 9·1 ; N, 15·3 per cent).

d-α-*Santalol.*—Santalal (3 g.) was dissolved in absolute alcohol (25 c.c.) containing aluminium ethylate (2 g.) and allowed to stand at room temperature for 4 days and then slowly refluxed on the water-bath for 5 hours. Alcohol was distilled off and the residue was heated with 10% potassium hydroxide (50 c.c.) for 15 minutes and extracted with ether and distilled in vacuum. α-Santalal distilled at 143°/5 mm. ; b. p. 158°/10 mm., 148°/5 mm., 143-44°/3 mm. ; n^{25}_{D}, 1·5013 ; d^{25}_{25}, 0·9970 ; $[R_L]_D$ 66·4 ; Calc. $C_{15}H_{24}\sqrt{\overline{1}}$ = 65·93 ; α_{5780} = +9·6° ; α_{5460} = +11·1° ; unsaturation value 1·00 ; strychine salt of hydrogen phthalate, m.p. 145° (Found : C, 81·52 ; H, 10·58. $C_{15}H_{24}O$ requires C, 81·8 ; H, 10·9 per cent).

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STRYCHNINE AND BRUCINE. PART VI.

MONONITROSTRYCHNINE

By Rafat Husain Siddiqui and Syed Khader Basha

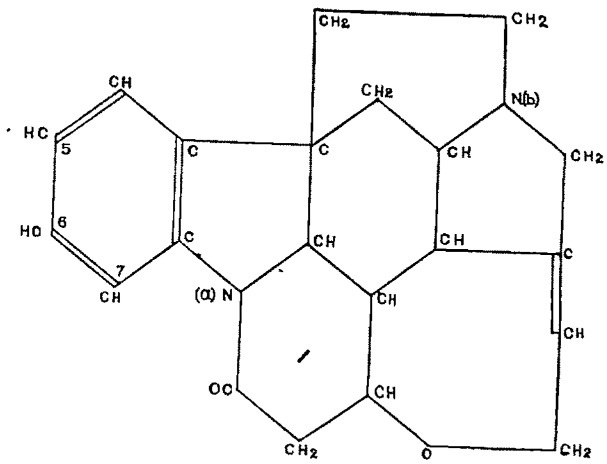
Mononittostrychnine is prepared from sttychnine nitrate and gives aminostrychnine on reduction. Both bases give crystalline salts and the nitro group is unaffected by acid and alkaline hydrolysis. Mononitrostrychnine, monoaminostrychnine and some salts have been tested for fungicidal activity with negative results.

The action of nitric acid on strychnine (*Gazzetta*, 1878, **8**, 82 ; *Ber.*, 1881, **14**, 774 ; *J. prakt. Chem.*, 1907, **75**, 122 ; *Compt. rend.*, 1883, **96**, 585 ; *J. Chem. Soc.*, 1885, **47**, 139 ; *J. Indian Chem. Soc.*, 1940, **17**, 152) has been the subject of a number of publications as a result of which a number of products have been characterised, which have contributed their part in the elucidation of the constitution of strychnine molecule. Tafel's dinitrostrychnine hydrate nitrate (*Ber.*, 1893, **26**, 333 ; *Annalen*, 1898, **301**, 285) was proved by Siddiqui (*Proc. Indian Acad. Sc.*, 1940, **11A**, 268) to be dinitrostrychnic acid. In connection with this work a publication of Loebisch and Schoop (*Monatsh*, 1885, **6**, 844), attracted the attention which describes the preparation of mononitrostrychnine and its conversion into an isomer on treatment with alcoholic potassium hydroxide. From this it appears that the isomer is mononitrostrychnic acid which furnishes a potassium salt and is formed by the cleavage of the cyclic amide group of the strychnine molecule.

To decide this a study of the substance was undertaken.

In this investigation mononitrostrychnine has been prepared from strychnine nitrate which gives monoaminostrychnine, m. p. 280°, on reduction. Both the bases give crystalline salts. Mononitrostrychnine in acid solution on basification with sodium and potassium hydroxides give their salts and the base is only recovered when the solution is neutralised with ammonia or sodium carbonate. The formation of alkali salts is a peculiar behaviour and resembles those of nitrophenols. The bases from the alkali salts are obtained by a method described under experimental. Mononitrostrychnine is not isomerised by treatment with alcoholic potassium hydroxide but gives a base identical with it. The nitro group is firmly bound and is unaffected by acid and alkaline hydrolysis. The exclusive formation of one mononitrostrychnine from strychnine nitrate is a case of migration of the nitro group from the basic nitrogen (b) to some place in the molecule while its stability points to its substitution in the benzene nucleus but at the same time other possibilities cannot be ruled out and the exact position

will only be fixed by degradative experiments. In dinitrostry chnine the nitro group occupy positions 5 and 7 of the benzene nucleus as proved by Robinson and others (*J. Chem. Soc.*, 1930, 830; 1931, 733; 1932, 780; 1933, 486), and if in this case also the nitro group enters the nucleus then it appears probable that it occupies position 5 and we have to visualise the strycnnine molecule in such a way that the pyrrolidine nucleus containing the basic N (b) is so orientated or folded round an axis due to its dynamic condition that the linkages are not disturbed and the *trans* configuration of the two nuclei containing the basic N (b) and the non-basic N (a) is maintained and that it offers a closer proximity for migration or jumping of the nitro group from the basic N (b) to position 5 of the benzene nucleus.



Mononitrostrychnine, its hydrochloride and the potassium salt, aminostrychnine and its hydrochloride were also tested for fungicidal activity by the spore germination test (*vide* Experimental). There was 89-100 percent germination while in solution mononitrostrychnine, monoaminostrychnine and its hydrochloride in 1 : 1000 concentration some mould was found to grow profusely. It appears probable that in low concentrations strychnine does not act as a germicidal to fungi.

EXPERIMENTAL

Strychnine Nitrate.—Dilute nitric acid (2% and 4%) was used when the former was found better as the latter gave increased yield of dinitrostrychnine. Strychnine (50 g.) was dissolved in dilute nitric acid (2%, 400 c.c.) by warming on the water-bath. Undissolved strychnine was filtered and the filtrate on cooling deposited strychnine nitrate in needles. The filtrate from this was used again to dissolve undissolved strychnine till it all went into solution, yield 50 g. (81%). The nitrate is soluble in water and chars at 280°. The mother-liquor from the nitrate on evaporation to dryness on the water-bath gave dinitrostrychnine (9 g.) which on reduction with zinc and hydrochloric acid yielded diaminostrychnine, m.p. 287° and gave no depression with an authentic specimen (Siddiqui, m.p. 287°; Hanriot, m.p. 265°, Leuchs and Krönke, m.p. not below 300°).

Mononitrostrychnine and its Salts.—Strychnine nitrate (33 g.) was dissolved in concentrated sulphuric acid (330 g.) by maintaining a temperature below 20°. tThe red solution after keeping for 8 days was diluted with water (80 parts) and was hen made alkaline with ammonia when it yielded the precipitate of mononitrostry

chnine which was washed with water, yield 29 g. (93%). It crystallises from acetone in prisms, m.p. 245° (Loebisch, m.p. 225°). In a second preparation basification of the solution was done with sodium hydroxide (30% aqueous solution) when a yellow precipitate appeared which dissolved in water on washing. The solution after making acid with hydrochloric acid (10%) was evaporated to dryness and the residue was taken up in dilute acetic acid (10%). The solution on neutralisation with aqueous sodium hydroxide gave a deep yellow precipitate which dissolved very little in chloroform and benzene (soluble fraction in prisms was identical with mononitrostrychnine). To recover the base from the yellow sodium salt it was dissolved in alcoholic hydrochloric acid and refluxed for 1 hour on the water-bath when sodium chloride separated which was filtered. The solution was further refluxed for 2 hours. The solvent was then removed and the residue was dissolved in water and the clear solution was divided into two portions, one being neutralised with ammonia and the other with sodium carbonate solution, the products from both were identical with mononitrostrychnine. It is soluble in acetone, benzene and alcohol and readily in chloroform. The combined fractions were fractionally recrystallised into six fractions when first two melted at 245° and the next two at 243-44°, the fraction fifth at 242° and the last at 238° and none gave any depression on admixture. The mother-liquor on complete removal of the solvent yielded a negligible quantity of an impure base which decomposed below 200°. (Found in material dried at 100°: C, 66·91 ; H, 6·00 ; N, 10·8. Calc. for $C_{21}H_{21}O_2N_2.NO_2$: C, 66·49 ; H, 5·54 ; N, 11·08 per cent).

The hydrochloride was obtained by adding ethereal hydrogen chloride to a solution of the base in chloroform. It was soluble in acetone, alcohol and water and crystallised from alcohol-ether in light yellow needles, which shrink and stick to the sides at 250°.

The picrate in benzene solution was obtained as an amorphous powder. It is sparingly soluble in alcohol and water. It chars and has no definite m.p. below 300°. [Found in substance dried at 100° : N, 12·8. $C_{21}H_{21}O_2N_2NO_2.C_6H_2.(NO_2)_3(OH)$ requires N, 13·8 per cent].

The chloroplatinate was obtained as a cream-coloured powder on mixing aqueous solution of the hydrochloride and the platinic chloride. It is insoluble in alcohol and water and does not melt below 300°. [Found in anhydrous material: Pt, 17·73. $(C_{21}H_{21}O_2N_2 \cdot NO_2 \cdot HCl)_2 \cdot PtCl_4$ requires Pt, 17·6 per cent].

The aurichloride was prepared by mixing aqueous solutions of gold chloride and the hydrochloride as a yellow powder. It is soluble in acetone and has m.p. 242° (decomp.). (Found in material dried at 100° :Au, 28·4. $C_{21}H_{21}O_2N_2 \cdot NO_2.HCl.AuCl_3$ requires Au, 27·4 per cent).

The Nitrate—To an alcoholic solution of the base an alcohol-ether solution of nitric acid was added when the nitrate came down in needles which do not melt below 300°. It is soluble in water and difficulltly in alcohol.

Attempted Hydrolysis of Mononitrostrychnine with Alcoholic-Potassium hydroxide.—Mononitrostrychnine was refluxed with 25% alcoholic potassium hydroxide on a sand-bath for 25 hours. The bright red solution on concentration gave ruby-red crystals which become yellow on complete removal of the solvent. The salt was refluxed with alcoholic hydrochloric acid (10%) for 6 hours and the separated potassium chloride was filtered. The solvent was removed and the residue was dissolved in water. The clear solution on basification with ammonia gave a base, m.p. 245° which gave no depression when mixed with mononitrostrychnine. This shows the stability of the nitro group. The nitro group is not removed on treatment with alkali nor the cyclic amide group is ruptured by this treatment. The experiment further shows that the alkali treatment does not isomerise mononitrostrychnine and the product obtained on reduction yields monoaminostrychnine.

Reduction of Mononitrostrychnine : Monoaminostrychnine.—The various fractions were reduced but in every case an identical product was obtained. Nitrostrychnine (0·9 g.) with zinc and hydrochloric acid (50 c.c., 50%) was slightly warmed on the water-bath. When brisk evolution of hydrogen commenced the mixture was removed from the water-bath. The reduction was complete in 15 minutes. The solution was filtered and decomposed with sodium hydroxide (30%). The precipitate and the filtrate were shaken with chloroform. The solution was washed with water and dried over anhydrous sodium sulphate. On removal of the solvent monoaminostrychnine crystallised in glistening plates, m.p. 280° (Leobisch, m.p. 275°). When the solution after reduction was not worked up at once and was allowed to stand, the base was coloured and the impurity was got rid of with great difficulty. (Found in material dried at 100° : C, 71·91 : H, 6·76 ; N, 11·91. Calc. for $C_{21}H_{21}O_2N_2{\cdot}NH_2$: C, 72·2 ; H, 6·59, ; N, 12·03 per cent).

The dihydrochloride was prepared by adding chloroform solution of the base to an excess or hydrogen chloride in ether when it came down as a sticky precipitate. It crystallised from alcohol-ether in long needles with a violet tinge, and does not melt below 300°. It is soluble in alcohol, acetone and water.

The chloroplatinate separated in aggregates of needles with a brownish tinge on mixing an aqueous solution of the hydrochloride and platinic chloride. It does not melt below 300°. On warming a pinch in water a pink to violet solution is produced. [Found in material dried at 100° : Pt, 25·4. $(C_{21}H_{21}O_2N_2{\cdot}NH_2{\cdot}2HCl)_2.\ 2PtCl_4$ requires Pt, 25·7 per cent].

The dipicrate separated when chloroform solution of the base was added to a solution of picric acid in chloroform-ether. It was well washed with ether and crystallised from chloroform-petroleum ether in red needles, m.p. 265°. It is soluble in acetone, chloroform, alcohol and water. [Found in material dried at 100° : N, 15·6. $C_{21}H_{21}O_2NH_2{\cdot}2\ [C_6H_2{\cdot}(NO_2)_3(OH)]$ requires N, 15·83 per cent].

Fungicidal properties.—Fungicidal properties of the following five substances were tested by the Imperial Mycologist by the spore-germination test. Viable

spores of *Ustilago kolleri* Wille were used for the purpose. The results are given below.

Substance.	1 : 500	1 : 1000	1 : 2500	1 : 5000	1 : 7500
	Concentrations				
A. Mononitrostrychnine ...	97	97	100	96	100% germination
B. Mononitrostrychnine hydrochloride ...	89	94	99	99	99% ,,
C. Potassium salt of mononitrostrychnine ...	93	96	96	99	100% ,,
D. Monoaminostrychnine hydrochloride ...	94	94	90	98	100% ,,
E. Monoaminostrychnine ...	97	93	98	99	99% ,,

B. C. and D were dissolved in water and A and E in dilute acetic acid and all were diluted with water. In solution of A, D and E in 1 : 1000 concentration some mould was actually found to grow profusely.

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PHYSICO-CHEMICAL STUDIES ON HAEMOLYSIN, PART II.

pH AND HEAT STABILITY OF HAEMOLYSIN.

BY S. S. DE,

The effect of p_H and of heating has been determined on crystalline haemolysin. It has been found that haemolysin is most stable at p_H 6·0 and the critical inactivation temperature of haemolysin is observed to be 62°.

The effect of hydrogen-ion concentration and heat on the activity of various crystalline enzymes have been extensively studied and are of importance in determining the characteristics of an enzyme. There are some enzymes which are very sensitive to variations in p_H and temperature while others are not so much affected. These observations might lead to some conclusions as to the nature of the bond involved in the structure of the protein molecule. In some cases it has been observed that in moderately alkaline solution an enzyme is inactivated, but again on neutralising it the activity is partially restored. The active enzyme which is termed a colloidal complex is broken up in alkaline solution and recombines on neutralising the solution.

Heat also inactivates enzymes, but while some enzymes are very sensitive even to a temperature of 50°, others are not much affected even at a temperature of 80°. So a term has been introduced called the half inactivation temperature at which the activity of the enzyme is reduced to one-half of the original value within 60 minutes. The effect of hydrogen-ion concentration and of heating has been determined on crystalline haemolysin (De, *Ann. Biochem. Expt. Med.*, 1944, **4**, 45). which has been found to be enzymic in nature.

EXPERIMENTAL

Effect of p_H. For the purpose of determining the effect of pH on the activity, 0·2% solution of once-crystallized haemolysin from *Naja Tripudians* (variety monocellate) was made in normal saline. 5 C.c. of this solution were transferred to each of a number of flasks and adjusted to different p_H values by the addition of hydrochloric acid or caustic soda solution. For adjusting to p_H 1 and 13, equal volume of 0·2 N acid or alkali were respectively added to the haemolysin solution.

The volume in the different flasks was made up to 10 c.c. by dilution with normal saline. The activity was determined immediately and afterwards at definite intervals of time, the solutions being kept all the time in the refrigerators at 4°. Before determining the activity, the different solutions were brought to p_H 7·4 and then dilutions were made with physiological saline. The units of haemolysin contained

in the different flasks were determined after intervals of 24 hours, 3 days and 6 days. For this purpose a fresh haemolysin solution was prepared each day and activities present in the different flasks were calculated in per cent of the original. To test whether alkali-denatured haemolysin can be reactivated, 50 c.c. of the above haemolysin solution which was kept at p_H 13·0 for 72 hours was neutralised with hydrochloric acid to p_H 6·0 and kept in the refrigerator at 4° for a long period and its activity determined from time to time. But the denatured haemolysin did not regain even a negligible part of its original activity.

TABLE I

Effect of p_H on crystaline haemolysin.

p_H.	Activity present in % of the original 24 hours	3 days	9 days
1·0	94	85	70
3·0	97	90	82
4·5	98·5	96	92
6·0	100	99	98·5
7·5	95	85	68
9·0	90	68	45
13·0	82	48	22

TABLE II

Effect of heat on crystalline haemolysin.

Temp.	Activity in % of the original
50°	76·3
60	54·6
62	50·2
70	23·8
80	8·5

Effect of Heating.—For studying the effect of heating, the same 0·2% solution of crystalline haemolysin from *Naja Tripudians* (variety monocellate) was used and the p_H of the solution was adjusted to p_H 6·0. 10 C.c. portions were transferred to different test tubes, and they were heated at different temperatures for a period of 60 minutes. The solutions were cooled and their activity determined with respect to the original venom. It was found that the activity was about half destroyed at 62°.

For purpose of comparison a 0·2% solution of crude *Naja Tripudians* (variety monocellate) venom was heated at 62° for 60 minutes and its activity determined. But instead of diminished activity its activity was slightly enhanced and found to be 101·5% in comparison with crude venom.

The crystalline haemolysin solution which was inactivated at 62° for 60 minutes was kept in the refrigerator at 4° for 24 hours and the activity of the sample was then determined. It was found that the inactivated product regained a portion of its original activity. The activity of the sample was 52·6% of the original, against its initial activity 50·2% of the original. Thus an increase of 2·4% of the total activity has been obtained by keeping the heat inactivated product in the cold.

It is observed that crystalline haemolysin is most stable at p_H 6·0 and is inactivated both in acid or alkaline solution. The rate of inactivation in the alkaline solution is much greater than in comparable concentration of acid solution. On neutralising alkali-inactivated solution, no regaining of the activity was observed.

Heating also inactivates haemolysin to a moderate degree and half-inactivation temperature of crystalline haemolysin was found to be 62°. But the haemolysin in crude venom was not inactivated by heating at 62°, rather the activity was slightly increased. This is probably due to the fact that some other inert protein, which is acting as an inhibitor, is absorbed on haemolysim molecules in crude venom, and the inert protein protects the haemolysim molecules from the effect of heat, it being denatured preferentially to the haemolysin.

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PHYSICO-CHEMICAL STUDIES ON HAEMOLYSIN. PART III.

ISO-ELECTRIC POINT OF HAEMOLYSIN

BY S. S DE

The iso-electric point of crystalline haemolysin has been determined both by the micro-cataphoretic method and the U-tube method and has been found to be at p_H 8·55 by the first method and 8·61 by the second method.

Of the different properties which characterise an enzyme; the determination of the iso-electric point is of considerable importance. Every protein molecule has a charge, which depends on the reaction of the medium in which it is dissolved. The p_H at which the charge of the protein is practically nil is called the iso-electric point of the protein. The iso-electric point coincides with a minimum for many of the physico-chemical properties of a protein, including cataphoresis, conductivity, solubility and osmotic pressure. The iso-electric point is affected by the buffer used for the measurement, since the charge on a colloidal particle may be affected not only by hydrogen ion but also by other ions present. It is known that if a protein solution is shaken with colloidal particles, the particles adsorb the protein and possess the same charge as that of the protein. It has been shown by Loeb (*J. Gen. Physiol.*, 1923, **6**, 105) that iso-electric point of gelatine or of egg-albumin, measured either when in solution or adsorbed on the surface of microscopic particles, gives fairly concordant results. Abramson (*ibid.*, 1932, **15**, 575) also compared his results for the electric mobility of serum albumin adsorbed on quartz surface and

measured by the microscopic method of electrophoresis and the data of Tiselius (*Nova acta reg. Soc. Sc., Upoaliensis*, 1930, 7, No 4) for the same protein in U-tubes and found approximate agreement between the mobilities obtained by the two methods. He, however, noticed that the iso-electric point shifted slightly due to adsorption.

Recently, Moyer (*J. Biol. Chem.*, 1937, 122, 641) showed that the electric mobility of horse-serum, pseudoglobin adsorbed on collodion particles, was the same as the electric mobility of the protein in the dissolved state. For determining iso-electric point the protein is generally coated on collodion or quartz particles and the charge of the particle is observed at different p_H values. The point at which the charge shifts from the positive to negative is taken to be the iso-electric point of the protein in the above medium. The buffer index is also used in determining the iso-electric point of a protein. A definite amount of protein is mixed with buffer solutions of different p_H values and p_H of the buffer, which shows the minimum shift from its original value, is taken to be the iso-electric point of the protein. In the cataphoretic method the iso-electric point is determined by studying the movement of the protein solution in a U-tube in an electric field. The iso-electric point of crystalline haemolysin (De, *Ann. Biochem. Exptl. Med.*, 1944 4, 45) has been determined by the cataphoretic method using a solution of the haemolysin itself and a suspension of quartz particles coated with the haemolysin. The iso-electric points observed in both the experiments were found to agree fairly with each other.

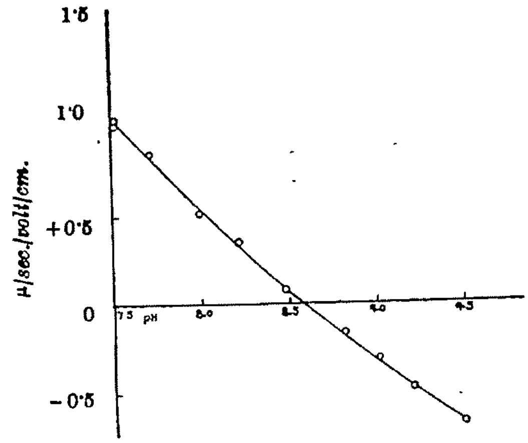
EXPERIMENTAL

Micro-cataphoretic Method.—A standard amount of aqueous suspension of quartz (Abramson, *J. Gen. Physiol.*, 1929, 13, 169) was placed in contact with stock crystalline haemolysin solution and after a few minutes the solution was diluted by the addition of a buffer solution so that the resultant buffer mixture had an ionic strength of 0·02*M*. The buffer solutions were those prescribed by Sorenson. Phosphate and borate buffers were used between p_H 6·0 and p_H 7·8 and p_H 8·0 and p_H 9·6 respectively. The final protein concentration was 0·2 per cent. The cataphoretic velocity of the quartz particles was observed in a flat rectangular cell of the Abramson type ("Electrokinetic Phenomena", Chemical Catalog Co., New York, 1934). The p_H of the different solutions was verified by measurement with glass electrodes and the specific conductance of each solution was measured by a Wheatstone bridge. The iso-electric point of haemolysin as determined by this method was 8·55 (Fig. 1).

Cataphoretic Method (U tube).—The apparatus consists of a U-tube with stop-cock on each side and at the same height. Also there is a side-tube of narrower bore, connected to the bottom of the U-tube. This is also provided with a stop-cock. A 0·1% crystalline haemolysin in *N*/15-borate buffer is poured into the side-tube, so that the U-tube is filled up to the lower ends of the stop-cocks. The stop-cock in the side-tube was then closed. The bore of each stop-cock was filled with

buffer solution of the same concentration as was used for dissolving the haemolysin by closing the other stop-cock and pouring the buffer solution carefully from the top of the tube.

FIG. 1.



Electric mobility curve of crystalline haemolysin.

The upper ends of the U-tubes were washed thoroughly with water and equal volumes of bufferèd solutions were placed on both ends. Connections were made with agar bridge to copper sulphate solutions to which copper-electrodes were dipped. A milliammeter was introduced in the circuit. The U-tube was fitted by a clamp and the stop-cocks opened and the current allowed to pass for a definite interval of time. The stop-cocks were then closed. The liquids in the upper ends of the tubes were transferred to two flasks and haemolytic activity was determined in both of them.

TABLE I

Electro-cataphoresis of haemolysin solution.

	Units of haemolysin	
*p*H.	Cathode-tube.	Anode-tube.
8·5	240	less than 10
8·56	72	" " 10
8·61	18	16
8·65	less than 10	66
8·70	" " 10	180

The iso-electric point as measured by the first method was found to be at *p*H 8·55 and by the second method at 8·61, which is within the limits of experimental error.

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STUDIES IN LONG-CHAIN ACIDS. PART VI. ON ALEURITIC ACID

By P. C. Mitter, Munindra Chandra Sen-Gupta and Amalendu Bose

A geometrical isomer of aleuritic acid has been obtained while attempting the synthesis of aleuritic acid.

Mitter and Mukherji (*J. Indian Chem. Soc.*, 1942, **19**, 303) have synthesised ω-methoxy-Δ^9-hexadecenoic acid which is an intermediate product in their intended synthesis of aleuritic acid. The work has now been extended by the present workers leading to the synthesis of a geometrical isomer of aleuritic acid, according to the following scheme:—

$$CH_3O{\cdot}(CH_2)_6{-}CH{=}CH{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (I)$$

$$Cl(CH_2)_6{-}CH{=}CH{\cdot}(CH_2)_7{\cdot}CO_2H \quad \ldots \quad (II)$$

$$Cl(CH_2)_6{-}CH{=}CH{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (III)$$

$$CH_3CO{\cdot}O(CH_2)_6{-}CH{=}CH{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (IV)$$

$$CH_3CO{\cdot}O{\cdot}(CH_2)_6{-}CHOH{-}CHOH{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (V)$$

$$OH(CH_2)_6{\cdot}CHOH{\cdot}CHOH{\cdot}(CH_2)_7{\cdot}COOH \quad \ldots \quad (VI)$$

It was originally proposed to convert the methoxy ester (I) into the correponding bromo-acid by treatment with hydrobromic acid. The procedure led, however, to extensive decomposition of the methoxy ester. The replacement of the OMe by chlorine could be conveniently effected by heating with hydrochloric acid (*d* 1·19) in a sealed tube. The chloro-acid (II), obtained in an excellent yield, was esterified and converted into the acetoxy ester (IV) by treatment with potassium acetate in glacial acetic acid. The acetoxy ester (IV) could be converted into the corresponding dihydroxy compound (V) by oxidation with perhydrol in glacial acetic acid solution. Hydrolysis with alcoholic potash gave a geometrical isomer of aleuritic acid (VI).

The acid, obtained by this method, was found to melt at 125° after two crystallisations from ethyl acetate, while the acid obtained from natural sources melts at 101°. A mixture of the two acids melted also at 101°. The natural acid forms an acetone compound and therefore it possesses the two contiguous OH groups in *cis*-configuration. The synthetic acid is therefore presumably the *trans*-variety. Attempts at its conversion into the *cis*- form are in progress.

Experimental

Ethyl 16-Chloro-Δ^9-hexadecenoate (III).—The methoxy ester (I) (2·5 g.) with 3 c.c. of glacial acetic acid and 10 c.c. of fuming hydrochloric acid, was heated in a glass tube in a bomb furnace at 160-80° for 6 hours. After cooling, the product was poured into cold water, extracted with ether, the ethereal layer washed with water, dried over anhydrous sodium sulphate and the ether distilled off. As the free acid could not be obtained in a sufficiently pure condition for analysis it was esterified with absolute alcohol and sulphuric acid in the usual way, poured into ice-water and extracted with ether. The ethereal layer was washed with sodium bicarbonate solution, then with water, dried and the ether removed. The residue distilled at 184°/5 mm. (Found: C, 68·5; H, 10·5; Cl, 10·6. $C_{18}H_{33}O_2Cl$ requires C, 68·2; H, 10·4; Cl, 11·2 per cent).

Ethyl 16-Acetoxy-Δ^9-hexadecenoate (IV).—A mixture of the dry chloro-ester (3·6 g.), fused potassium acetate (4 g.) and glacial acetic acid (14 c.c.) was refluxed on an oil-bath at 120-130° for 40 hours. A crystal of sodium iodide was added to the reaction mixture. On the completion of the reaction the product was poured into ice-water, extracted with ether and the ethereal layer washed successively with water, sodium bicarbonate solution and then with water and finally dried over calcium chloride. After removal of the ether, the residue

distilled at 185-90°/3 mm., yield 2 g. (Found: C, 70·9; H, 10·3. $C_{20}H_{36}O_4$ requires C, 70·6; H, 10·6 per cent).

Ethyl 16-Acetoxy-9:10-dihydroxyhexadecoate (V).—Perhydrol (9·4 g.) was taken in glacial acetic acid (34 g.) distilled over chromic acid and heated for one hour at 80°. After cooling the mixture to room temperature the acetoxy ester (4·5 g.) was added and the mixture shaken. The temperature of the mixture rose rapidly without the application of heat reaching a maximum of 70°. After cooling to room temperature, it was allowed to stand overnight. Acetic acid was next removed by steam distillation and the residue cooled and extracted with ether. The ethereal layer was washed and then dried with calcium chloride. On removal of the ether, a pale yellow viscous liquid remained which was presumably the desired compound (V). As it could not be obtained sufficiently pure for analysis, it was hydrolysed to the free acid.

ω:9:10-*Trihydroxyhexadecoic acid* (VI).—The above acetoxy ester (3 g.) was refluxed with alcoholic caustic soda (3 g. NaOH in 30 c.c. alcohol) for 6 hours. The alcohol was then removed by heating on the water-bath with the addition of successive small amounts of water. The solution was then cooled with ice and acidified with ice-cold dilute sulphuric acid. The acid separated as a pale yellow coloured solid. It was filtered, washed and dried. It was purified by two crystallisations from ethyl acetate. The final product was colourless. It did not decolourise bromine. The melting point was found to be 125° and it did not rise on further crystallisation. The mixed m. p. with natural aleuritic acid was found to be 101°. (Found: C, 63·28; H, 10·45. $C_{16}H_{32}O_5$ requires C, 63·15; H, 10·52 per cent).

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PHOTOCHEMICAL FORMATION OF HYDROGEN PEROXIDE FROM WATER. PART II. IN PRESENCE OF BASIC ZINC CARBONATE AND OXIDES OF CADMIUM, TIN AND THORIUM

By C. Narasimha Chari and M. Qureshi

The phofochemical formation of hydrogen peroxide from water has been found to take place in presence of basic zinc carbonate. A study of this reaction in presence of zinc carbonate and zinc oxide in the ultra-violet light from a mercury-vapour lamp has shown that zinc carbonate is more photoactive than zinc oxide in this reaction. Besides cadmium oxide which is already known to sensitise this reaction (*vide* 'Chemical Action of Light' by N. R. Dhar, p. 263), stannic oxide and thoria have also been found to act as photosensitisers. A comparative study of the photoactivity of these three oxides has been carried out.

In a previous communication (*vide* Part I of the present series, *J. Indian Chem. Soc.*, 1944, **21**, 97) it has been described that as a result of the photosensitising activity of zinc oxide, prepared by different methods, it was found that oxide prepared from carbonate by ignition has the greatest activity. This led to the idea that zinc carbonate itself might prove to be a sensitiser for the photochemical formation of H_2O_2 from water.

A number of tests for the detection of minute amounts of hydrogen peroxide are described in the literature. On examination, however, it was found that some of them were not as sensitive and specific as they were claimed to be. The following tests were finally employed for the detection of hydrogen peroxide in this investigation.

(*i*) The brown solution of ferric chloride (0·4%) and potassium ferricyanide (0·8%) is decomposed by reducing agents with the formation of Prussian blue. Hydrogen peroxide reduces ferricyanide to ferrocyanide which reacts with ferric chloride present to form Prussian blue. The limit of identification is known to be about $0 \cdot 08 \times 10^{-6}$ g. of hydrogen peroxide. This test could not be employed in the case of those test solutions which contained stabilisers because many organic substances were capable of reducing ferricyanide.

(*ii*) A neutral solution of potassium iodide containing starch is coloured blue due to the liberation of iodine in the presence of small quantities of hydrogen peroxide. The limit of identification has been found to be about $0 \cdot 03 \times 10^{-6}$ g. of hydrogen peroxide. Although this test is fairly sensitive, it is given by ozone as well as NO_2. The action of O_3 or H_2O_2 on potassium iodide, however, renders the solution alkaline, while the action of NO_2 in small concentration leaves it neutral. Consequently the presence of hydrogen peroxide or ozone is detected by adding a suitable indicator, such as cresol red, to a potassium iodide solution (*vide* McMorris and Dickinson, *J. Amer. Chem. Soc.*, 1932, **54**, 4248).

(*iii*) Hydrogen peroxide causes a yellow colour to develop in acidic solutions of titanium sulphate (0·2%). This test is a specific test for hydrogen peroxide though not very sensitive. The sensitivity is about $1 \cdot 24 \times 10^{-6}$ g. of hydrogen peroxide.

Experimental

In a few preliminary experiments, aqueous suspensions of zinc carbonate (basic carbonate C. P., Merck) each containing about 0·2 g. of the powder in 30 c. c. of conductivity water in presence and absence of a small amount of stabiliser such as phenol or glycerol, were exposed in open pyrex flasks to sunlight for a period of about five hours. After exposure the contents of the flasks were filtered and the filtrates were divided into four portions and tested for H_2O_2 employing the tests mentioned above.

Hydrogen peroxide was detected. Similar experiments carried out with stannic oxide, thoria and cadmium oxide revealed the presence of hydrogen peroxide, after exposure to

sunlight. The observations led the authors to undertake a detailed study of the sensitising action of the above mentioned powders, employing artificial ultraviolet light, in addition to sunlight. Cadmium oxide has been observed by previous workers to act as a sensitiser in this reaction as already mentioned in our previous communication, but as far as the present authors are aware, no detailed study of this sensitiser has been carried out in this connection.

Preparation of Sensitisers

Zinc carbonate was prepared by precipitating an aqueous solution of zinc sulphate with a solution of sodium carbonate. The resulting precipitate after washing was dried at 100°. In addition to this sample, Merck's C. P. basic zinc carbonate was also employed. Two samples of cadmium oxide were obtained from the sulphate and the nitrate respectively by precipitation with alkali and igniting the resulting powders at 500°. The colour of the two samples was chocolate-red. Stannic oxide was prepared by precipitating a cold aqueous solution of stannic chloride with ammonia, and thorium dioxide from the corresponding nitrate by precipitation with alkali. The resulting samples were ignited at 1000°. All the above powders were passed through 150 mesh.

The chemicals employed in the preparation of the above samples were Merck's "Guaranteed Reagents" or "Extra Pure" chemicals. The experimental details and the method of estimation of hydrogen peroxide, adopted in this investigation, were the same as those described in our previous communication (*loc. cit.*). The stabiliser used was either phenol or glycerol, the quantity employed being such that the solution was always 0·1 *M* with respect to the stabiliser.

The Sensitising Action of Zinc Carbonate and Zinc Oxide

(*i*) These experiments were performed with the object of comparing the sensitising activity of zinc carbonate and zinc oxide. For this purpose an aqueous suspension (conductivity water) of the powder containing phenol as a stabiliser was exposed to the total ultraviolet light from a mercury vapour lamp in a quartz flask, which was placed at a distance of 15 cm. from the lamp. The flask was shaken at intervals during illumination. The results are summarised in Table I in which c represents the amount of hydrogen peroxide formed in moles, M, Merck's sample, C.I., the sample of zinc oxide prepared from carbonate by ignition and S.P., the sample prepared from sulphate by precipitation.

TABLE I

Powder (0·1 g.), water (25 c.c.), phenol (0·1 *M*), exposed to total ultraviolet for 2 hours.

Powder	Zinc carbonate (M)	Zinc carbonate (S.P.)	ZnO (C.I.)	ZnO (S.P.)
$c \times 10^6$	1·63	1·15	1·10	0·83

TABLE II

Powder (0·2 g.), water (30 c.c.), phenol (0·1 *M*), exposed to sunlight for 9 hours.

Powder	Zinc carbonate (M)	Zinc carbonate (S P)	ZnO (S.P.
$c \times 10^6$	26·4	19·6	18 7

(*ii*) In these experiments aqueous suspensions of the powder were exposed in open Pyrex flasks to sunlight. After a period of 9 hours the flasks were removed and the hydrogen peroxide content of each was estimated. The results are shown in the following table.

The results as given in Tables I and II indicate that zinc carbonate supplied by Merck is more active than zinc oxide in sensitising this reaction. The sample of zinc carbonate that was prepared in the laboratory was comparatively less active than Merck's zinc carbonate.

Photochemical Formation of Hydrogen Peroxide from Water in presence of Oxides of Cadmium, Tin and Thorium

In the following experiments, the reaction was studied in the presence of powders mentioned above employing ultraviolet light from a mercury vapour lamp as well as sunlight. The results are given in Tables III to VI. In these tables the letters S.P. have the same significance as mentioned above, while N.P. indicate the sample prepared from nitrate by precipitation The quantities of H_2O_2, obtained when zinc oxide (S.P) was used as sensitiser, are also given for the sake of comparison.

TABLE III

Powder (0·1 g.), water (15 c.c.), exposed to light from a quartz mercury vapour lamp focussed by a glass condenser for 2 hours.

Powder	ZnO (S.P.)	CdO (S.P.)	CdO (N.P.)
$c \times 10^6$	0·5	0·4	0·3

TABLE IV

Powder (0·2 g.), water (30 c.c.), phenol (0·1 *M*), exposed in open Pyrex flasks to sunlight for 5 hours.

Powder	ZnO (S.P.)	CdO (S.P.)	CdO (N.P.)
$c \times 10^6$	12·55	1·65	1·35

TABLE V

Powder (0·1 g.), water (25 c.c.), phenol (0·1 *M*), exposed to total ultraviolet light from a quartz mercury vapour lamp for 6 hours.

Powder	ZnO (S.P.)	Stannic oxide	Thoria
$c \times 10^6$	1·86	0·71	0·38

TABLE VI

Powder (0·2 g.), water (30 c.c.), phenol (0·1 *M*), exposed to sunlight for 9 hours.

Powder	ZnO (S.P.)	Stannic oxide	Thoria
$c \times 10^6$	18·7	5·1	0·7

The results shown in Tables III and IV indicate that cadmium oxide prepared from sulphate is more active than that prepared from nitrate, as in the case of zinc oxide. The brown coloured oxide gradually turned white during exposure. It can also be seen from the above tables that the photoactivity of the oxides of cadmium, tin and thorium is much less than that of zinc oxide.

DISCUSSION

Iodide test is one of the most sensitive tests for H_2O_2, but as this test is also given by NO_2 and O_3, particular care has to be taken to eliminate the possibility of the existence of traces of the latter substances, while employing this test for the detection of small quantities of H_2O_2. NO_2 is best detected by Griess Ilosva reaction which consists in the formation of red colouration on the addition of an acetic acid solution of sulphanilic acid and α-naphthylamine to the test solution. O_3 is best detected by its bleaching action on a dilute alkaline solution of fluorescein. The importance of carrying out these elimination tests in an investigation like the present one is emphasised by the following observation made during the course of this investigation. While carrying out preliminary tests with different sensitisers it was observed that the filtrate from an exposed sample containing aqueous suspension of Merck's Cr_2O_3 gave an instantaneous colouration with a neutral starch-iodide solution. The sample

kept in the dark also behaved in a similar manner. On carrying out elimination tests, both the filtrates were found to contain traces of NO_2, but no H_2O_2, or O_3, indicating that the sample of Cr_2O_3, was contaminated with some nitrite. A pure sample of Cr_2O_3, prepared by us, never gave a positive test with starch-iodide solution.

Incidentally, the above observation gave rise to the idea that the reaction between nitrite and iodide is probably catalysed by traces of chromium chloride and chromium sulphate, which were found to be present in the above filtrates.

Zinc carbonate supplied by Merck was found to be much more active than the sample of zinc carbonate prepared in the laboratory. This is apparently due to the fact that the average size of the particles in the case of Merck's sample was smaller than that of the particles in the sample prepared by the authors, but it may also be due to a difference in the chemical composition of the two samples of zinc carbonate, as the latter is known to possess a variable composition depending upon the conditions of its preparation. The extent to which each of the two factors is responsible for the observed difference in sensitising power cannot, however, be decided unless special care is taken to use powders having particles of the same average size.

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STUDIES IN LONG-CHAIN ACIDS. PART VII

By P. C. Mitter and Munindra Chandra Sen-Gupta

Attempt has been made to synthesise ambrettolic acid by Bouveault reduction of the half ester of Δ^6-tetradecene-1 : 14-dicarboxylic acid.

Kerschbaum (*Ber.*, 1920, **60**, 902) isolated the odoriferous principle of muskkernel oil and showed it to be the lactone of a hydroxy unsaturated acid, namely ambrettolic acid (I). The lactone, known as ambrettolide (II), possesses a strong smell of musk.

$$CO_2H{\cdot}(CH_2)_5{-}CH{=}CH{\cdot}(CH_2)_7{\cdot}CH_2OH \quad \ldots \quad (I)$$

$$\underbrace{CO{-}(CH_2)_5{-}CH{=}CH{\cdot}(CH_2)_7{\cdot}CH_2}_{O} \quad \ldots \quad (II)$$

Ambrettolic acid was shown to be 16-hydroxy-Δ^7-hexadecenoic acid and ambrettolide, the corresponding lactone.

On catalytic reduction of the acid and the lactone the corresponding dihydro compounds, both possessing a strong smell of musk, were obtained. The dihydro compounds have been synthesised by Ruzicka and Stoll (*Helv. Chim. Acta*, 1928, **11**, 1159) and also by Chuit and Hauser (*ibid.*, 1929, **12**, 463).

Mitter and Bhattacharyya (*J. Indian Chem. Soc.*, 1942, **19**, 69) have synthesised 16-hydroxy-Δ^9-hexadecenoic acid and also its lactone, starting from aleuritic acid. This acid, which differs from ambrettolic acid in having the positions of the terminal groups reversed, has been named epi-ambrettolic acid.

Epi-ambrettolide, the corresponding lactone, possesses a strong smell of musk, showing that the interchange of the terminal functional groups does not materially affect the odour of the product.

We have tried to synthesise ambrettolic acid and ambrettolide by an extension of the work of Mitter and Bhattacharyya along the following lines :—

$$OH{\cdot}CH_2{\cdot}(CH_2)_5{\cdot}CH{=}CH{-}(CH_2)_7{\cdot}CO_2H \quad \ldots \quad (III)$$

$$\rightarrow OH{\cdot}CH_2{\cdot}(CH_2)_5{-}CH{=}CH{-}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (IV)$$

$$\rightarrow OH{\cdot}CH_2{\cdot}(CH_2)_5{\cdot}CHBr.CHBr{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (V)$$

$$\rightarrow CO_2H{\cdot}(CH_2)_5{\cdot}CHBr{\cdot}CHBr{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (VI)$$

$$\rightarrow CO_2H{\cdot}(CH_2)_5{\cdot}CH{=}CH{\cdot}(CH_2)_7{\cdot}CO_2Et \quad \ldots \quad (VII)$$

The conversion of (V) into (VI) by the oxidation of the-CH_2OH to-COOH group offerred certain difficulties. Oxidation under mild conditions led to the formation of 15-aldehydo-Δ^9-pentadecenoic acid. The ester acid (VII) could only be obtained under very specific conditions. Bouveault reduction of (VII) to (I) has not yet been achieved for want of sufficient material.

Hydrolysis of (VII) gives rise to Δ^6-tetradecene 1 : 14-dicarboxylic acid.

Experimental

Ethyl 16-Hydroxy-Δ^9-hexadecenoate (IV).—Dry epi-ambrettolic acid (10 g.) was added to a mixture of absolute alcohol (50 c.c.) and concentrated sulphuric acid (*d* 1·84, 3 c.c.) and the mixture refluxed on the water-bath for 24 hours. It was then poured into ice-water, extracted thoroughly with ether, the ethereal layer washed successively with dilute sodium carbonate solution and water. The residue after drying and removal of the solvent distilled at 198-200°/3·7-4mm. (Found : C, 72·33; H, 10·96. $C_{18}H_{34}O_3$ requires C, 72·49; H, 11·40 per cent).

Ethly 16-Hydroxy-9 : 10-dibromohexadecenoate (V).—A solution of bromine (1·06 g.) in glacial acetic acid (10 c.c.) was added with constant shaking to a solution of epi-ambrettolic ester (1·7 g.) in glacial acetic acid (20 c.c.). The dibromo ester could not be isolated in a pure state since it liberated bromine even on distillation in vacuum. It was used as such for the oxidation experiments.

15-Aldehydo-Δ^9-pentadecenoic Acid.—Acetic acid (15 c.c.) was added to the above solution and then a solution of CrO_3 (0·9 g.) in 80 % acetic acid (10 c.c.) was added to it drop by drop, the temperature of the mixture being maintained at 80-85° by heating on the water-bath. The addition required about 3½ hours. When the reaction was over, zinc dust (9 g.) was added to it and the mixture heated on the water-bath for 2½ hours more to complete the debromination. It was then filtered and the filtrate extracted thoroughly with ether. The ethereal layer was washed with water and the solvent removed after drying. The residue was hydrolysed with alcoholic potash (20 c.c., 10%) by refluxing on the water-bath for 5 hours. The alcohol was removed on the water-bath by evaporation after addition of successive portions of water. It was then extracted with water to remove neutral matter and then the ice-cold alkaline solution was acidified with cold dilute sulphuric acid. The brownish white precipitate which separated was filtered, washed and dried and crystallised from a mixture of ethyl acetate and petroleum ether and then twice from petroleum ether (b. p. 50-60°) yielding an aldehyde, which is perfectly colourless, m. p. 40-41°. (Found: C, 71·1; H, 9·7. $C_{16}H_{28}O_3$ requires C, 71·6; H, 10·4 per cent).

Δ^6-Tetradecene-1 : 14-dicarboxylic Acid.—Epi-ambrettolic acid (8 g.) was dissolved in glacial acetic acid (75 c.c.) by warming slightly on the water-bath. The solution, after cooling was brominated with a solution of bromine (1·75 c.c.) in 25 c.c. of glacial acetic acid. After allowing to stand for some time, the mixture was heated on the water-bath and a solution of CrO_3 (4·6 g.) in 80% acetic acid (25 c.c.) was added to it drop-wise in course of 4 to 5 hours. The mixture was then heated on the boiling water-bath for another hour and then debrominated by heating with zinc dust (25 g.) on the water-bath. The filtrate on dilution with water deposited a solid which was filtered, washed, dried and recrystallised twice from petroleum ether (b. p. 60-70°). It melts at 75-76°. (Found: C, 67·3; H, 9·4. $C_{16}H_{28}O_4$ requires C, 67·6; H, 9·9 per cent).

Ethyl Hydrogen-Δ^6-tetradecene-1 : 14-dicarboxylate (VII).—Epi-ambrettolic ester (12 g.) was dissolved in acetic acid (50 c.c.) and brominated with a solution of bromine (2·5 c.c.) in acetic acid (50 c.c.) and then oxidised with CrO_3 (6 g.) in 80 per cent acetic acid (40 c.c.) as in the previous experiments. It was debrominated with zinc dust (30 g.) at 90-100°. The product was filtered and the filtrate diluted with a large volume of water when the ester-acid separated as an oil. It was taken up with ether and the ethereal layer washed with water to remove chromium salts, dried with anhydrous sodium sulphate and the solvent removed. No solid derivative of the ester acid could be prepared. A portion was hydrolysed with alcoholic potash in the usual way when Δ^6-tetradecene-1 : 14- dicarboxylic acid was obtained.

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THE COMPOSITION OF THE FATTY ACIDS OF THE SEED FAT OF *LOPHIRA ALATA* (OCHNACEÆ)

By M. A. Saboor

The mixed fatty acids of the oil from the seeds of *Lophira alata* (Ochnaceæ) have been separated by the usual methods into solid (41·9%) and liquid acids (58·1%). The fatty acids have been calculated to be palmitic (23·2%), stearic (0·3%), arachidic (4·8%), behenic (4·9%) lignoceric (6·9%), palmitoleic (11·7%), oleic (8·3%), linoleic (31·5%), eicosenoic (2·1%), docosenoic (5·6%) and unsaponifiable matter (0·7%).

The fat is obtained from the decorticated seeds of *Lophira alata* (Ochnaceæ). The tree is not indigenous to India but found extensively in tropical Africa from where the present sample was procured. The tree amongst others supplies the so-called African oak. The fat from the seeds of this tree is sometimes called Niam fat (Schweinfurth, *Botan. Ergeb. der ersten Niam*-Niam Reise; *Bull. Imp. Inst.*, 1909, **7**, 367). It is also called Meni oil in Sierra Leone and Zawa oil in Egyptian Sudan. Natives in certain localities in tropical Africa (Heckel, *Les Graines grasses nouvelles ou peu connues des colonies francaises*, Paris, 161) use it for culinary purposes and also as a hair oil. The oil has also been suggested as suitable for soap-making and the residual oil cake as suitable for fertiliser (Anon., *Bull. Imp. Inst.*, 1935, **33**, 286)

A number of workers have recorded constants for this oil. Thus according to Lewkowitsch (*J. Soc. Chem. Ind.*, 1907, 1265) the oil has the following characteristics: Specific gravity at 40°, 0·9016-0·9044; S.V., 182-195; I.V., 70-72·5; R.M.V., 0·8-0·9; unsaponifiable 0·5-9·0%; Titer, 47° to 49°.

The seeds from Sierra Leone, Sudan and Uganda have been examined by the Imperial Institute, London (Anon., *Bull. Imp. Inst.*, 1908, **6**, 243, 366; 1912, **10**, 226; 1935, **33**, 284). The data of the fat from different localities are compared with those of ours in the table given below.

Characteristics.	Present sample.	Sierra Leone.	Sudan.	Uganda.
Sp gr. 100/15°	—	0·859	—	0·8604
Sp. gr. 40/40°	0·9021	0·9016-0·9105	0·9063	—
M. p. (open tube)	27·0°	—	—	24·5°
Ref. Index at 40°	—	—	—	1·4610
Acid value	—	18·54-48·0	5·78	7·0
Sap. value	191·6	180·7-195·6	190·1	187·9
Iod. value (Wij's)	73·4	—	—	73·2
Iod. value (Hübl)	—	68·0-72·5	78·12	—
Unsaponifiable	0·7	0·5-2·5	1·38	1·3
Titer	—	45·0-49·0°	42·5°	43·8°
R.M.V.	0·7	—	—	—

The constants of the present sample therefore do not materially differ from those of the previous workers. Pickles and Hayworth (*Analyst*, 1911, **36**, 493) have gone further into the question and besides the usual characteristics, which also do not materially differ from those of ours, investigated the fat by semi-quantitative methods. Thus they have separated the solid and liquid acids by lead salt-ether method and found that the saturated (solid) acids and unsaturated (liquid) acids are present in equal proportions. They have further subjected the solid acids to fractional crystallisation from alcohol and isolated and identified arachidic and palmitic acids though no quantitative data regarding these two acids have been given. There were indications that besides these two acids other components are present in the solid acids. The liquid acids had an iodine value of 139. They have identified linoleic and oleic acids in the liquid acids and on the basis of iodine value conclude that these two acids are present in

about equal proportions. They have not stated how they have estimated these two acids in presence of one another.

In the present work, following the Twitchell method of lead salt separation as modified by Hilditch (Hilditch, "The Chemical Constitution of Natural Fats," 1941, reprinted, p. 371) it has been found that the saturated (solid) and unsaturated (liquid) acids are 41·9 and 58·1 per cent respectively. The iodine value (3·81) of the saturated (solid) acids esters shows that the separation of the saturated from the unsaturated fatty acids is fairly good. In view of the absence of the iodine value data of the solid acids of Pickles and Hayworth it is not possible to judge the extent of the separation of the saturated from the unsaturated acids but it must be presumed, in view of the method available at that time (1911), that separation had not been complete and considerable quantity of certain unsaturated acid or acids has passed into the solid acids. This might explain the reason why equal proportion of solid and liquid acids was obtained.

So far as the liquid acids of Pickles and Hayworth were concerned, they stated, basing their argument on the iodine value (139), that oleic and linoleic acids occurred in equal proportions. This is a fallacy and as such cannot be admitted. It presupposes that oleic and linoleic acids are the only constituents of the liquid acids and that no other acid or acids are present in the liquid acids. This has, however, not been shown. If, on the other hand, certain unsaturated acids pass into the solid acids and certain amount of saturated acids passes into the liquid acids of which there is ample evidence, there may be more than one way of building up an iodine value of 139. The average molecular weights or in other words the saponification equivalents of solid and liquid acids are of prime importance in coming to any conclusion. The present investigation fully corroborates that C_{16} mono-ethenoid (palmitoleic) is one of the major components of the liquid acids. The work confirms the presence of palmitic (23·2%) and arachidic (4·8%) acids as saturated fatty acids and oleic (8·3%) and linoleic (31·5%) as unsaturated fatty acids in this fat. Besides, by systematic fractionation of the methyl esters of the solid and liquid acids separately through 'E.H.P. Column' as employed by Hilditch *et al* (*loc. cit.*) and determination of S.E. and I.V. of various fractions, the following acids have been calculated in additon to those already stated : (1) stearic (0·3%), (2) behenic (4·9%), (3) lignoceric (6·9%), (4) palmitoleic (11·7%), (5) eicosenoic (2·1%) and (6) erucic (5·6%).

EXPERIMENTAL

Characteristics

For determination of characteristics standard text-books have been followed.

Consistency—White solid melting to a clear liquid with slightly yellowish colour having unpleasant smell and taste. M. p. 27°; Sp. gr. at 40°, 0·9921, S.E. 292·8; I.V. (Wij's), 73·4; R.M.V., 0·7; unsaponifiable matter, 0·7 (since S.V.×S.E.=56,100 S.V.=191·6).

Separation of Saturated and Unsaturated Fatty Acids

The fat (552 g.) was extracted with potassium carbonate solution in order to make it free from acids. The potassium soap after acidification gave free acids (57 g.) and the neutral fat remained (495 g.). In view of the small quantity of the free acids and possibility of decomposition of the acids involved no further investigation was undertaken. The acid-free fat (99 g.) was resolved into the following groups according to the method of Twitchell as modified by Hilditch (*loc. cit.*).

			Corresponding esters.	
			S.E.	I.V.
Solid acids ...	40·4g.	41·9%	299·4	3·81
Liquid acids ..	... 56·0	58·1	293·4	136·80

The iodine values show that the separation of saturated from the unsaturated fatty acids is quite satisfactory.

Fractionation of Methyl Esters.—The methyl esters of solid acids (36·8 g.) and those of liquid acids (50·5 g.) were prepared as usual, of which 31·8 g. and 49·2 g. were taken separately for systematic fractionation through 'E.H.P. column' as described by Hilditch. The tables below summarise the complete fractionation data for the component acids of this fat. The composition of each ester fraction has been calculated from its S.E., I.V. and weight.

Fractional distillation of methyl esters of solid acids
(31·75 g. distilled through "E.H.P. column")
Pressure during distillation maintained between 0·1—2 mm.

No.		Temperature of Oil-bath	Column Middle	Column Head.	S.E.	I.V	Saturated C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	Unsaturated E_{18} (Ol)	N S
S1	3·27g.	185-190°	152-158°	118-120°	271·6	1·0	3·06	0·17	—	—	—	0·04	—
S2	3·70	190°	158°	120-122°	270·6	0·7	3·61	0·06	—	—	—	0·03	—
S3	3·75	192°	156°	121°	270·4	1·1	3·69	0·01	—	—	—	0·05	—
S4	3·84	195°	156°	121 118°	270·3	1·4	3·78	—	—	—	—	0·06	—
S5	3·42	195-200°	156-170°	118° falling	272·9	6·7	3·15	—	—	—	—	0·27	—
S6	4·29	200-225°	170-200°	165°	324·2	9·5	—	—	3·51	0·30	—	0·48	—
S7	3·44	225-260°	200°	165° falling	352·2	1·7	—	—	0·05	3·32	—	0·07	—
S8	5·50	Residue	Residue	Residue	411·8*	5·3*	—	—	—	—	5·12	—	0·38
	31·21				Wt.		17·29	0·24	3·56	3·62	5·12	1·00	0·38
					% Esters		55·4	0·8	11·4	11·6	16·4	3·2	1·2
					% Acids		55·8	0·8	11·6	11·8	16·8	3·2	—

* S_8 Esters freed from unsaponifiable matter ("N—S"), S.E. 383·8, I.V., 0·1.

Fractional distillation of methyl esters of the liquid acids.
(49·22 g. distilled through "E.H.P. column")
Pressure during distillation maintained between 0·1—2 mm

No.		Temperature of Oil-bath.	Column Middle.	Column Head.	S.E.	I.V.	Calculated composition of ester fractions. Unsaturated C_{16}	C_{18} (Ol)	C_{18} (Li)	C_{20}	C_{22}	N-S
L1	3·41g.	220°	210°	110-124°	276·5	99·5	2·27	0·84	0·30	—	—	—
L2	3·45	220°	206°	124°	285·8	126·7	1·08	0·86	1·51	—	—	—
L3	4·21	220·223°	206°	124°	288·4	144·8	0·88	0·56	2·77	—	—	—
L4	5·22	223°	206°	124-125°	290·2	150·3	0·75	0·67	3·80	—	—	—
L5	6·04	223°	206-207°	125°	290·4	148·9	0·84	0·89	4·31	—	—	—
L6	6·67	223-235°	207°	124-125°	289·7	148·8	1·08	0·87	4·72	—	—	—
L7	10·33	235-247°	207-210°	125-129°	286·5	146·7	2·83	0·54	6·96	—	—	—
L8	3·37	247-249°	215°	129-130°	302·7	129·9	—	0·57	1·80	1·00	—	—
L9	5·78	Residue	Residue	Residue	358·4*	99·5*	—	—	0·12	0·80	4·66	0·20
	48·48				Wt.		9·73	5·80	26·29	1·80	4·66	0·20
					% Esters		20·1	12·0	54·2	3·7	9·6	0·4
					% Acids		20·0	12·0	54·5	3·8	9·7	—

* L9 Esters freed from unsaponifiable matter ("N—S"), S.E. 346·2, I.V. 75·2.

Identification of Fatty Acids (Arachidic and Behenic acids).—The solutions left over after determination of S.E. of the fractions S_6 and S_7 were acidified and the solids so obtained were separately crystallised from petroleum ether (b p. 60—80°). Crystals from S_6, melting at 75° when compared with an authentic sample of arachidic acid show no depression of m.p. Similarly the crystals from S_7 melt at 82°. An authentic sample of behenic acid could not be obtained and its comparison therefore could not be undertaken.

Linoleic Acid.—A part of the liquid acids was brominated when a crystalline tetrabromostearic acid was obtained, m. p. 114°.

Various practical difficulties intervened in isolation and recognition of other fatty acids. So far as palmitic, oleic etc. are concerned their isolation and recognition are not of special importance since they have been reported in practically every instance so far encounterned. Similarly, palmitoleic acid is now known to be a constituent of nearly all natural fats but in vegetable kingdom it is known to be a subordinate component. Its isolation is therefore important so far as the present work is concerned. Unfortunately, however, we have not had enough material to undertake this aspect of the question. This aspect of the question along with the glyceride structure of the fat will form a separate communication when sufficient material is obtained.

Calculated Composition of Fatty Acids

Acids. Saturated :		"Solid" acids S (41·9%).	"Liquid" acids L (58·1%.	Total.	% Fatty acids (including unsaponifiable). (Wt.)	(Mol).
n-Hexadecanoic, Palmitic	(C_{16})	23·21	—	23·21	23·2	25·8
n-Octadecanoic, Stearic	(C_{18})	0·32	—	0·32	0·3	0·3
n-Eicosenoic, Arachidic	(C_{20})	4·78	—	4·78	4·8	4·3
n-Docosenoic, Behenic	(C_{22})	4·86	—	2·86	4·9	4·1
n-Tetracosenoic, Lignoceric	(C_{24})	6·88	—	6·88	6·9	5·3
Unsaturated :						
$\Delta^{9:10}$-Hexadecenoic, Palmitoleic	(C_{16})	—	11·66	11·66	11·7	13·1
$\Delta^{9:10}$-Octadecenoic, Oleic	(C_{18})	1·34	6·95	8·29	8·3	8·4
$\Delta^{9,10,12:13}$-Octadecadienoic, Linoleic	(C_{18})	—	31·52	31·52	31·5	32·0
Eicosenoic (probably $\Delta^{11:12}$)	(C_{20})	—	2·15	2·15	2·1	2·0
Docosenoic (probably $\Delta^{13:14}$), Erucic	(C_{22})	—	5·58	5·58	5·6	4·7
Unsaponifiable	—	0·51	0·24	0·75	0·7	—

The fat is extremely rich in palmitic, palmitoleic and linoleic acids. The most interesting feature of this fat is the presence of so high a proportion of palmitoleic acid (11·7%), which has hitherto been known as a very subordinate component in land flora. It cannot be classed as a semi-drying oil inspite of linoleic acid content of 31·5%, since the iodine value on the whole fat is only 73·4. It must be classed as a non-drying oil and the best use that can be suggested for it is not as a direct soap-making material but as a diluent in the various oils and fats used in soap manufacture since the soap that will be formed by the mixed fatty acids of the oil is likely to be hard.

The author has experienced a great deal of difficulties while performing these experiments specially for the want of a suitable 'Hyvac' pump during ester fractionation and a Tesla Coil for determining the order of the vacuum. He wishes to express his thanks to the Principal of the College for giving him all facilities as far as possible under the existing circumstances and further to Prof. S. N. Bose of the University of Dacca for valuable help and guidance in calculating the ester fraction data.

THE DACCA INTERMEDIATE COLLEGE,
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PHYSICO-CHEMICAL STUDIES ON HAEMOLYSIN. PART IV. MOLECULAR WEIGHT OF HAEMOLYSIN

BY S. S. DE

The molecular weight of haemolysin has been found to be 31,900 by the diffusion method, a value which agrees well with the values of 31,000—41,000 in Svedberg units. The value also tallies fairly well with values obtained by other methods.

There are various methods of determining the molecular weight of protein. Among them mention may be made of osmotic pressure, diffusion, and rate of sedimentation in an ultracentrifuge. The diffusion method has been used for determining the molecular weight of crystalline haemolysin (De, *Ann. Biochem. Expt. Med.*, 1944, **4**, 45) the process adopted for this purpose was that of Northrop and Anson.

If two solutions of definite concentrations are separated by a porous membrane, solute from the more concentrated solution passes to the dilute solution, and the diffusion coefficient is defined in the following way :

$$D=\frac{dq}{Adt\frac{dc}{dx}} \quad \dots \quad (1)$$

where D is the diffusion coefficient, dq is the quantity which passes across the plane of area A in time dt under a concentration gradient of dc/dx.

Suppose a solution of concentration c_1 is separated from a more dilute solution of concentration c_2 by a porous membrane through the pores of which the solute can diffuse. The solute will diffuse from c_1 to c_2. If the volumes of these solutions are large and the experiment is conducted for a short duration, the concentrations will remain constant.

Let the effective area of the pores be A and the effective length be h. The concentration gradient will then be constant and equal to c_1-c_2/h and the quantity q diffusing in time t will be :

$$q=DAt\frac{c_1-c_2}{h} \quad \dots \quad (2)$$

or

$$D=\frac{hq}{At(c_1-c_2)}.$$

If the solution is pure solvent, c_2 is zero.

Then

$$D=\frac{hq}{Atc_1}.$$

Dimensions of D.—Since concentration may be expressed as quantity per unit of volume, the units used to measure the quantity cancel out provided the same unit is used to express the concentration as is used to measure the quantity diffusing. If time is expressed in days and length in centimetres, then

$$D=\frac{h\text{ cm}}{A\text{ cm}^2}\,\frac{q\text{ units}}{t\text{ days}\frac{q_1\text{ units}}{\text{cm}^3}}=\frac{hq.\text{ cm}^2}{A.q_1.t\text{ day}}$$

in which q_1 is the number of units per c.c. of the concentrated solution. If the amount contained in 1 c.c. of the concentrated solution is taken as the unit of quantity, *i.e.* if $q_1=1$ and

the amount diffused is expressed in this unit (*i.e.* as the number of c.c. of the concentrated solution containing the quantity diffused) then

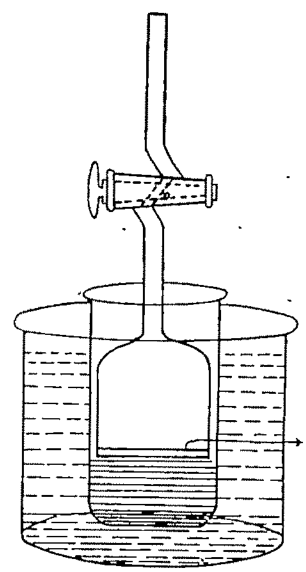
$$D = \frac{hq(\text{c.c.})\text{cm}^2}{At \text{ day}} = \frac{kq(\text{c.c.})\,\text{cm}^2}{t \text{ day}}$$

where q (c.c.) is the number of c.c. of the concentrated solution that contains the amount of substance diffused. For any membrane, the effective thickness and area may be assumed constant and therefore h/A is constant and may be called K, the membrane constant. In order to obtain this value, the apparatus should be standardised against a solution, the diffusion constant of which is known.

EXPERIMENTAL

Apparatus.—The diffusion cell used is shown in Fig. 1. It is suspended in a closely fitting beaker by a rubber tube. It consists of sintered glass fused at one end of the cell. The diaphragm was of G—4 dimensions. After the cell was tested for leaks, the volume of the diffusion cell up to the glass stop-cock was determined by weighing the empty cell and then filled with distilled water. The cell was first cleaned by sucking water, freed from dissolved gas by boiling, through the porous disc, with a water pump at the upper end. The liquid was expelled by applying pressure at the same end. The cell was then rinsed with the solution, the diffusion coefficient of which is to be measured through the diaphragm, and filled completely without bubbles past the stop-cock which was then closed. The cell was then immersed in a beaker of water for washing and the last drop of adherent water was removed by tilting the disphragm and touching it with a glass rod. The cell after removal of the adherent liquid was suspended by 15 cm. long rubber tube in a clean beaker containing a quantity of water equal to the volume of the cell. The suspension was so adjusted that the disphragm was accurately horizontal against a mercury surface The apparatus was then placed in a water bath at 7°. The amount of solute diffused was never allowed to exceed 3% of the total in the concentrated solution.

FIG. 1



Diffusion cell.

Standardisation of Diffusion Membrane.—The membrane constant K which is the ratio of the thickness of the membrane to its effective area was calculated from data obtained by allowing solutions of HCl and maltose (the diffusion coefficients of which are known and which are extrapolated from Oholm's data) to diffuse through the membrane for a given length of time at a constant temperature 7°.

The membrane constant K may then be calculated by substitution in the formula,

$$K = \frac{Dt}{q(\text{c.c.})}$$

where q (c.c.) is the number of c.c. of the concentrated solution that contains the amount diffused in the time t expressed in days. D=known diffusion coefficient of the substance in solution.

TABLE I

Determination of membrane constant K at 7°

Solution.	Time in days.	Equivalent c.c. diffused.	q (c.c.) per day.	Average q (c.c.) per day.
HCl 0·1 N	0·0347	0·390	11·24	
	0·0417	0·472	11·32	
	0·0417	0·473	11·34	11·29
	0·0486	0·548	11·27	
Maltose 10%	0·333	0·469	1·408	
	0·375	0·508	1·355	
	0·417	0·578	1·386	1·385
	0·500	0·696	1·392	

Diffusion coefficient for 0·1 N-HCl at 7° = 1·88 cm^2 per day extrapolated from Oholm's data. Therefore K = 0·166. Diffusion coefficient for 10% maltose at 7° = 0·23 cm^2 per day extrapolated from Oholm's data. K from this is 0·172. So the mean K, the cell membrane constant is 0·169.

Diffusion Coefficient of Haemolysin.—Twice crystallised haemolysin, freed from salt by dialysis, was used for this experiment. Determination of diffusion coefficient was made with two different concentrations of haemolysin. For this purpose a 2% and 5% solution of haemolysin were diluted separately with an equal volume of 0·1M phosphate buffer of p_H 6·2 to give 1% and 2·5% solution of haemolysin in 0·05 M phosphate buffer (p_H 6·2). 30 C.c. of 0·05M phosphate buffer of the same p_H was placed in the beaker. Then the cell was suspended in the beaker containing the buffer and allowed to diffuse for a definite period. The whole arrangement was placed in a refrigerator at 7° and the beaker containing the buffer was immersed in water contained in a beaker also maintained at 7°. The solvent containing the diffusate was quantitatively removed and its activity and protein content determined. The density of haemolysin was determined by the displacement of xylene at 7°.

TABLE II

Determination of diffusion coefficient of haemolysin at 7°

Haemolysin solution.	Time in days.	Haemolysin diffused as c.c concentrated solution: Activity.	Protein.	D (Haemolysin) cm²/day: Activity	Protein.
1% p_H 6·2	1·0	0·343	0·340	0·0580	0·0575
	1·5	0·514	0·520	0·0580	0·0586
	1·5	0·508	0·515	0·0573	0·0580
2·5% p_H 6·2	1·0	0·345	0·344	0·0583	0·0581
	1·5	0·516	0·508	0·0581	0·0573
	1·5	0·510	0·515	0·0575	0·0580
				Mean 0·0579	0·0579

Calculation of the Radius and Molecular Weight of Haemolysin from the Diffusion Coefficient.—According to Einstein (*Z. Elektrochem.*, 1908, **14**, 235) the diffusion coefficient is related to the radius of the particle by the following equation :

$$D=\frac{RT}{N}\;\frac{1}{6r\pi\eta}$$

where $R=8\cdot3\times10^{7}$ erg $\text{deg}^{-1}\,\text{mole}^{-1}$; $T=280°$ (abs) for $7°$; $N=6\cdot06\times10^{23}$ mole^{-1} ; r=radius of the particle including water of hydration in cm ; η=viscosity of water at $7°$ $=0\cdot01422$ erg sec. cm^{-3}

$$D=\frac{1\cdot432\times10^{-13}}{r}\;\frac{\text{erg deg. mole cm}^3}{\text{erg deg. mole cm sec}}$$

$$=\frac{1\cdot432\times10^{-13}}{r}\;\frac{\text{cm}^2}{\text{sec}}=\frac{1\cdot237\times10^{-8}}{r}\;\frac{\text{cm}^2}{\text{day}}$$

$$r=\frac{1\cdot237\times10^{-8}}{D}\text{ cm}=\frac{1\cdot237\times10^{-7}}{\cdot00579}\text{cm}$$

$$=2\cdot136\times10^{-7}\text{ cm.}$$

The molecular weight of haemolysin may be calculated from the radius by the following equation :

$$M=\tfrac{4}{3}\pi r^3 gN$$

$$g=\text{density}=\text{g. cm}^{-3}\;[g\text{ (found)}=1\cdot29]$$

$$M=\tfrac{4}{3}\times3\cdot14\times6\cdot06\times10^{23}gr^3$$

$$=25\cdot4\times10^{23}gr^3$$

$$=25\cdot4\times10^{23}\times1\cdot29\times9\cdot74\times10^{-21}$$

$$=31{,}900.$$

The molecular weight of haemolysin thus determined is within the range of values (31,000-41,000) considered as the Svedberg unit (*Nature*, 1937, **139**, 1051). The minimum molecular weight of haemolysin has also been determined from the estimation of the various amino-acids (Part V). A fair correlation has been obtained between the two results, one obtained by the physical method and the other by the chemical method.

My best thanks are due to Dr. B. N. Ghosh for his keen interest and the facilities given to me.

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ESTIMATION OF NICKEL

By S. Sen

A simple, economic volumetric process for estimating nickel, specially in non-ferrous alloys, is described. It does not require keeping for completion of reaction nor any excess of reagent.

Amongst the methods generally followed for the estimation of nickel, the two more convenient and economical than others are (*i*) precipitation with dimethylglyoxime and weighing as its nickel salt or NiO ; (*ii*) separation of nickel with the above reagent and titration with NaOH after dissolving the precipitate in excess of H_2SO_4.

The first method is simple but necessitates addition of excess of the reagent and keeping for 15 minutes to 30 minutes at the boil; for complete precipitation and quick filtration of the Ni salt, standard methods (that of O' Brunck) suggest the use of 7 times, by weight of the reagent, that of the nickel salt theoretically, 1 molecule of Ni combines with two of dimethylglyoxime; therefore 4 times (weight) as much of the reagent as nickel is required.

The second method by Par and Lindgen, however, requires much practice. In case $N/10$-NaOH is used for back titration, it necessitates the use of $N/10$-H_2SO_4 for dissolving the nickel precipitate. In that case it requires warming of the solution and sometimes boiling. It has also been observed that sometimes minute specks of precipitate escape dissolution.

Temperature of the Ni solution (in sulphuric acid) is an important factor in final titration. There being no added indicator and the nickel solution itself functioning as one, this raising or lowering of temperature of the solution has much to do with the end-point. The end-point is more sharp above 60° than below it. Further increase in temperature does not show any improvement, on the contrary, too much increase more or less destroys the sharpness of the end-point.

The following is a simplified process for the estimation of nickel, specially in non-ferrous alloys. The process is essentially volumetric and does not require keeping for completion of reaction, nor any excess of reagent.

Procedure

Dissolve 0·2 g. of the sample in 50 c.c. of nitric acid, evaporate nearly to dryness and then take up in 50 c.c. of water. Filter off any precipitate of tin. In the filtrate pass H_2S to separate copper and lead or electrolyse with Pt electrodes. Make up the volume of the filtrate to 200 c.c. (after boiling off H_2S, if any), add 20 c.c. of 25% ammonium chloride solution, 10 c.c. of 20% citric acid solution, and 50 c.c. of ammonia. Warm to 55-60° for 5 minutes. Remove from the hot plate, add 5 c.c. of ammonia and titrate with 1% dimethylglyoxime solution. Use a filter paper soaked with dimethylglyoxime solution as an outside indicator. The red colour produced will gradually fade until it will be such as to be visible only in transmitted light. Addition of 3 to 4 drops more will cause disappearance of this colour. This point is taken as the end-point of the titration.

The dimethylglyoxime is similarly standardised against a known nickel or its salt. The following are some results in comparison with the standard precipitation method.

			Nickel found by the			
Experiment.		Ni taken.	titration.	precipitation.	difference.	% Error.
1	Nickel	0·0400 g.	0·03992 g.	0·03997 g.	0.00005	0·12
2	Nickel	0·0300	0·02994	0·02998	0·00004	0·13
3	Cupro-nickel	—	0·05195	0·05220	0·00025	0·50
4	White copper	—	0·02460	0·02449	0·00011	0·06
5	Nickel silver	—	0·02130	0·02120	0·00010	0·05
6	,,	—	0·02176	0·02140	0·00036	0·18
7	,,	—	0·02082	0·02080	0·00002	0·01
8	,,	—	0·02274	0·02260	0·00014	0·07
9	,,					
10	,,					

Interference

The main element that interferes with this method is copper. Even if the copper is kept in solution as cuprammonium, some dimethylglyoxime is used up in excess of that ordinarily consumed. This is due probably to the formation of a compound of copper with dimethylglyoxime as studied by Kolthoff (*J. Amer. Chem. Soc.*, 1930, **52**, 2222). This excess can be cut short by slow addition, yet a stage could be reached at which comparison could be made.

Iron in small amounts can be kept suppressed as citrate. The titration can be done in presence of zinc (which up to 40% did not interfere).

The titrations are best done in an automatic filling burette of the baryta type to avoid loss of alchohol due to evaporation.

The method is satisfactory for quick estimations, as well as for economical use of dimethylglyoxime, and can be used with considerable accuracy. A few estimations will enable the operator to detect the end-point correctly.

In presence of appreciable amount of iron, a faint colour is taken as the end-point as it requires 0·1 to 0·2 c.c. before it is completely decolourised, while in the absence of iron only 0·025 to 0·05 c.c. will give the end-point.

Recovery of Dimethylglyoxime from Nickel Precipitate

The method is economic and simple and saves the trouble of carrying out the complicated process of *breaking* with acid and regenerating dimethylglyoxime. The only reagent employed is a sulphureted hydrogen Kipp and a concentration or distillation arrangement.

Procedure.—The Ni precipitate is suspended in water and warmed. A rapid stream of H_2S is passed through it until cold. If the gas bubbles are not sufficient to effectively stir the suspended matter, a mechanical arrangement may be employed. The whole mass is then digested under pressure for nearly an hour. The filtrate is concentrated to get the dimethylglyoxime. It can further be purified by recrystallisation from alcohol.

The yield is satisfactory. A better yield is obtained if the whole operation is carried out in alcohol medium rather than water, with special arrangements to avoid too much loss of the suspending liquid.

The author expresses his indebtedness and thanks to the authorities of the Ordnance Laboratories for giving the facilities to undertake the above work.

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CAWNPORE,

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HEAT POLYMERISATION OF OILS

By N. L. Phalnikar and B. V. Bhide

Polymerisation of some of indigenous vegetable oils : safflower, niger seed and olive oils, has been studied with reference to cracking, The nature of the polymerised products and the acids of the lower molecular weights have been identified.

The subject of heat polymerisation has been studied by several workers (Wolf, *Fette. Chem. Umschau*, 1933, **40**, 113; Steger and Van Loon, *ibid.*, 1935, **42**, 217; Kino, *Sci. papers Inst. Phys. Chem. Res. Tokyo*, 1931, **16**, 127, 132, *et. seq*; Morell, *Chem. Ind.*, 1937, **73**, 1087; Kurz, *Z. angew. Chem.*, 1935, **48**, 3; Scheiber, *Fette. u. Seifen*, 1936, **43**, 103; Kienle, *J. Soc. Chem. Ind.*, 1936, **55**, 229; Bradley, *Ind. Eng. Chem.*, 1937, **29**, 440, *et. seq.*). These workers have studied the heat polymerisation by heating the oils at about 300° in presence of an inert gas to avoid oxidation. The progress of polymerisation was followed by determining the iodine value, refractive index, etc., the polymerised products were found to be far too complex for direct identification and therefore it has not been possible so far to establish any theory which accounts completely for the mechanism of polymerisation. However, it has been indicated that in the polymerisation the first stage is the cracking of the fatty acids at the point of the double bonds in the unsaturated acids; but no attempt has been made by previous workers to identify these products of cracking. Such an identification would lead to a better understanding of the mechanism of polymerisation.

We therefore intended to study the polymerisation of Indian vegetable oils and to study the nature of the products of cracking, as well as that of the polymerised products.

Safflower, niger seed and olive oils were chosen for this study because

(1) The component glycerides of these oils are known :

(2) Safflower and niger seed oils represent a typical class of oils containing linolic acid while olive oil represents another class containing oleic acid as the major component acids.

The heat polymerisation of these oils therefore will give an idea of the polymerisation of the glycerides of oleic and linolic acids. Simultaneously with this work the effect of heat on pure simple glycerides has also been studied as it will make the interpretation of these facts easier (Phalnikar and Bhide, *J. Univ. Bomay*, 1943, **11**, Part V, p. 77).

Experimental

The Physical Properties of the Oils.—Safflower and Niger seed oils used in this work were extracted by pressing the seeds (purchased from the local market, Poona district) in a country *Ghanee*. The olive oil used was a commercial sample available in the local market. These had the following physical and chemical constants.

Table I

Constant.	Safflower.	Niger.	Olive.
Refractive index at 30°	1·47287	1·46720 at 26°	1·46391.
Density	0·9669	0·9202	0·9170
Iodine value (I.V.) (Rosenmund and Kuhnehemm)	125·4	120·5	88·0
Saponification value (S. V.)	188·1	193·5	189·0
Acid value (A. V.)	2·439	2·0	1·0

Polymerisation of the Oils.—The oils were heated in a distilling flask with a naked flame under reduced pressure, the temperature of the oil being 360°-400°. The volatile liquid

products were condensed (distillate). Some CO_2 and a large amount of acrolein were evolved. The heating of the oils was discontinued as soon as frothing began to occur. The residue and the distillate were then analysed separately.

Methods of Analysis.—The distillate was separated into a neutral portion and an acid portion. The neutral portion was further separated into saponifiable and non-saponifiable portions. The saponifiable part was found to be an ester of oleic acid. The non-saponifiable part consisted mainly of saturated and unsaturated hydrocarbons with traces of ketones and alcohols. The probable constitution of the hydrocarbons was determined by oxidation and molecular weight determination. The acids of the acid portion were converted into methyl esters and fractionally distilled. The major portion of this distillate consisted of mixtures of acids (saturated and unsaturated) with less than twelve carbon atoms, and a small portion (high boiling) consisted mainly of the esters of oleic acid and acids of higher molecular weights. These high molecular weight acids (polymerised acids) could not be separated into homogeneous products by the usual methods of separation *viz.*, as lead and magnesium salts etc.

Analysis of the Residue.—The residue was saponified. The acids obtained were converted into methyl esters, fractionally distilled and the acids obtained from various fractions were found to be comlpex mixtures. Attempts were made to separate these complex mixtures into individual homogeneous acids by lead salt and magnesium salt methods but homogeneous products could not be obtained. The molecular weight and equivalent weight determinations show that the acids were monobasic and dibasic acids. Some of them contained a hydroxylic group also as shown by the acetyl value.

For the sake of brevity the analytical constants and other details have not been given. A summary of the results obtained has been given below.

Safflower Oil

The oil (500 g.) on distillation gave 80 g. of the distillate (16%), 400 g. of the residue (80%) and 20 g. of the gases—(4% by difference).

Myristic, palmitic, stearic and arachidic acids were identified in the solid acids of the distillate, while heptylic, pelargonic acids and an acid of equivalent weight 398·8 were the saturated acids (liquid) and oleic acid and an acid with 10 carbon atoms with a double bond at the fourth carbon atom were the unsaturated acids which were identified in the liquid acid portion of the distillate. From the saponifiable part of the neutral portion of the distillate, oleic acid was identified, thus showing that the saponifiable part of the neutral portion was some ester of oleic acid. In the unsaponifiable portion of the neutral fraction of the distillate, ketones, alcohols probably hydrocarbons of different molecular weights were found to be present.

The Residue.—The highly viscous residue on hydrolysis and subsequent fractionation of the methyl esters of the acids showed that most of the acids originally present in the oil were also present and in addition, acids of high molecular weights ranging from 380-584 were also found. Attempts to obtain homogeneous polymerised acids failed. Oxidation also did not give any definite result. These polymerised acids also possessed an acetyl value and are probably hydroxy unsaturated acids. This is in agreement with the views of Kurz Z. (*angew. Chem.*, 1936, **49**, 235). Some of these acids are monomeric and others dimeric. The nature of these acids appear to be similar to that of polymerised acids investigated by Bradley and co-workers (*loc. cit.*). Their stability to oxidation indicated the possiblity of their being ring

compounds. This view is supported by the work. of Farmer (*J. Chem Soc.*, 1934, 1940.), who has isolated six-membered ring compounds from the polymerisation of methyl sorbate.

Niger Seed Oil

Niger seed and olive oils have been similarly subjected to heat polymerisation. In each case the distillate and the residue were analysed as described above. The residue in the case of niger seed oil was first resolved into two fractions by acetone into an acetone-soluble part and the other, an acetone-insoluble part. Each portion was analysed separately as above. The results in both the cases were similar to those obtained above, hence for the sake of brevity details of identification have been omitted and the results are described briefly below.

Heat polymerisation of Niger seed Oil.—1150 G. of the oil on distillation at reduced pressure gave 287 g. (24·6%) of the distillate, 750 g. (65·3%) of the residue and 113 g. of gases (9·8% by difference).

Composition of the Distillate.—The distillate was separated into neutral portion and acid portion. The neutral portion consisted of a glyceride of oleic acid and a mixture of ketones and alcohols and probably hydrocarbons of different molecular weights. The acidic portion of the distillate was separated into solid and liquid acids. The solid acids identified were lauric, myristic, palmitic, stearic and traces of arachidic acids. The original oil also contains these solid acids. Caprylic acid accompanied by lauric, myristic and palmitic acids forms the major part of the "liquid" acids. Oleic acid and an acid with one double bond, probably at the fourth carbon atom, have been identified in the liquid unsaturated acids.

The Residue.—The brown and viscous residue was separated into acetone-soluble and acetone-insoluble parts. Both these parts were hydrolysed and the acids obtained were converted into methyl esters. The lower boiling fraction showed practically the same composition as that of the distillate. The methyl esters of higher molecular weights could not be distilled without decomposition. The acids had equivalent weight varying from 334 to 442, and molecular weight varying from 567 to 659. The equiv. wt. and mol. wt. of these acids indicate the presence of polymerised dibasic and monobasic acids. The acids were gummy and probably mixtures and had appreciable acetyl value indicating the presence of hydroxy acids.

Olive Oil

Heat polymerisation of Olive Oil.—138 G. of the oil on distillation at reduced pressure gave 110 g. of the distillate (nearly 80%), 19 g. of the residue (13·7%) and 9 g. of gases (6·3%) by difference.

Composition of the Distillate.—The neutral portion of the distillate was found to consist of ketones, alcohols and hydrocarbons of varying mol. wts., accompanied by traces of a glyceride of oleic acid. In the acid portion of the distillate, palmitic and stearic acids were identified, while pelargonic acid was identfied as the saturated liquid acid Moreover, oleic acid and other low mol. wt. acids of the type obtained in niger seed oil experiments were also identified.

The Composition of the Residue.—The residue was saponified and the acids obtained were separated into liquid acids and gummy acids. The liquid acid was identified as oleic acid. The gummy acid had equiv. wt. 305 and mol. wt. 464 thus indicating the presence of polymerised acids. The presence of hydroxy acids in the polymerised acids was also indicated by their high acetyl value.

DISCUSSION

As the major part of the distillate contains free saturated and unsaturated acids, a disruption of the glycerides must be taking place. This may be due either to the hydrolysis of the oil into glycerine and the free acids, or thermal decomposition of the triglycerides into acrolein and free acids.

Acids from the Distillates

The saponifiable part in the distillate is in a small quantity and hence the triglycerides are not distilling over in any appreciable quantity. The saponifiable part is likely to be an allyl ester of a fatty acid, as the smell of allyl alcohol was frequently noticed during saponfication and examination of the neutral portion.

Since low molecular weight acids, saturated as well as unsaturated, have been found in the distillate, thermal decomposition of the free acids, formed in the disruption of the triglycerides, must have been taking place to an appreciable extent.

The saturated low molecular weight acids have composition corresponding to C_7 and C_{10}. Assuming that the evidence collected is not so conclusive as to show the presence of individual acids, yet the presence of saturated low molecular weight C_7 and C_{10} acids cannot be doubted. This observation is the first of its kind. This further points out that cracking of the free fatty is followed to a certain extent by hydrogenation. Isolation of solid derivatives of these acids such as phenacyl derivatives is no doubt desirable but this necessitates the preparation of these acids in a pure condition and this was not possible as the quantities of the acids were small. The isolation of the amides and the I. V. and equivalent weights of the methyl esters give enough support for the conclusions drawn.

The low molecular weight unsaturated acids could not be identified as individual substances but oxidation experiments definitely point out the presence of unsaturated acids with equivalent weights corresponding to C_{10} acids containing one double bond, probably at the fourth carbon atom from the carboxylic group, as succinic acid was one of the oxidation products. As in the unsaturated acids originally present in the oil, the double bonds are at the 9, 10, 12 and 13th carbon atoms, a shift of the double bonds during heating must be occurring.

High molecular weight saturated acids in the distillate are only those that are present in the original oil. The formation of saturated acids with carbon atoms more than 12 during heating is entirely precluded.

It is significant that no trace of linolic acid is detected in the distillate ; an appreciable quantity of oleic acid is, however, detected and its presence has been proved beyond doubt.

Along with oleic acid, small quantities of acids possessing molecular weights higher than 300 have been detected.

Neutral Portion

The identfication of the neutral products is comparatively in a less satisfactory state. Unsaturated hydrocarbons, ketones and alcohols of varying molecular weights are undoubtedly present. No direct evidence for the presence of hydrocarbons could, however, be collected, but from the general properties it appears that they are present.

Residue

The residue presents a brown viscous product of a type similar to standard oils, possessing an appreciable A.V. and low I.V.

The residue can be separated into acetone-soluble and acetone-insoluble parts. The acetone-soluble part contains almost all the acids present in the oil, along with oleic acid and other high molecular weight acids, the molecular weights ranging from 300 to 567. The acetone-insoluble part resembles a gel and gives acids of high molecular weights (658).

In general, the residue contains the original solid acids, oleic acid and polymerised acids of high molecular weights. Their equivalent weights and molecular weights show that they are mixtures of monobasic and dibasic acids. All attempts to obtain homogeneous products have failed. These acids have acetyl value indicating the presence of unsaturated hydroxy acids. The stability towards oxidising agents shows that they are likely to be cyclic (Farmer, *loc. cit.*).

The main outcome of this work is the identification of low molecular weight acids. This has been done for the first time. When the other products of high molecular weight are identified the nature of these products will have to be taken into account in the final scheme of the mechanism of polymerisation.

Most of the earlier workers have tried to isolate polymerised acids in the pure condition. In this work also all such attempts have failed. Enough evidence has been obtained in the present work and also by earlier workers which proves the shifting of double bond in the heat treatment and these on polymerisation will lead to a greater number of polymerised isomers. These isomers will have closely similar properties and hence their isolation in the pure condition will be impossible because the free energy changes involved in the shifting of the double bond are likely to be very small and not very different for various positions. Bradley (*loc. cit.*) has recently reported the isolation of the pure dimer but it is very likely that it is a mixture of several isomers possessing closely allied properties. Oxidation experiments will reveal the type of the cyclic ring, *i.e.* whether it is a four membered or a six membered ring.

More chemical and physical evidence must be sought for. We are, therefore, carrying on experiments on pure simple glycerides such as triolein, trilinolin and trilinolenin.

The experimental part of this work was carried out by Messers J. D. Lagwankar and R. C. Shah.

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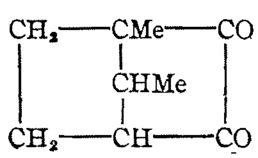
STUDIES IN THE CAMPHORQUINONE REARRANGEMENT. PART II. FORMATION OF 2:3-DIMETHYL*CYCLO*HEXAN-1-ONE-4-CARBOXYLIC ACID FROM SANTENONEQUINONE

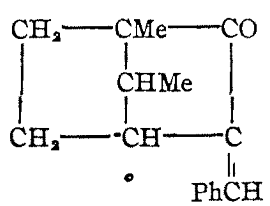
By Ram Narayan Chakravarti

Santenonequinone rearranges in presence of concentrated sulphuric acid to give 2:3-dimethyl*cyclo*hexan-1-one-4-carboxylic acid. The keto-acid has been degraded to a tricarboxylic acid, $C_8H_{12}O_6$, which has been identified with pentane-$\beta\gamma\epsilon$-tricarboxylic acid synthesised by an unambiguous method.

In a previous communication (Chakravarti, *J. Indian Chem. Soc.*, 1943, **20**, 301), the preparation of the racemic modification of 2:2:3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid from synthetic camphor by following the method of Samuel and Manasse (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831) was described. The properties of the above keto-acid (Chakravarti, *loc. cit.*, p. 303) were in excellent agreement with the view held by Simonsen and his co-workers (*J. Chem. Soc.*, 1925, 1295; 1927, 77) regarding the structure of the corresponding dextrorotatory keto-acid. Whilst experiments are in progress with a view to synthesising the racemic keto-acid of this structure, the properties of which are wholly inconsistent with those of a synthetic acid (Guha and Dasgupta, *J. Indian Inst. Sci.*, **22A**, XX, 255), it seemed desirable in the meantime to examine the behaviour of other substances, closely related to camphorquinone, towards sulphuric acid. The present communication, however, deals with the product derived from santenonequinone (I).

In the course of their work on teresantalic acid Semmler and co-workers (*Ber.*, 1907, **40**, 446; 1908, **41**, 125) prepared benzylidene santenone (II) which on oxidation with potassium permanganate in acetone solution yielded santenonequinone, m.p. 105°. A few years later, Palmen (*Finska Kemistamfundet Medd.*, 1927, **36**, 11; *Chem. Zentrl.*, 1927, II, 1691) obtained a quinone, m.p. 84-85°, having presumably the same structure by the action of hydrochloric acid on *iso*nitrososantenone (III) in presence of formaldehyde. It has been suggested (*cf.* Simonsen, The Terpenses, Vol. II, p. 220) that the two quinones must be stereoisomeric although no definite proof exists in support of this view.


(I)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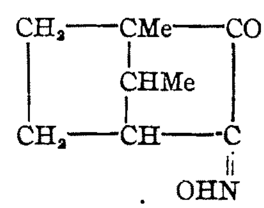
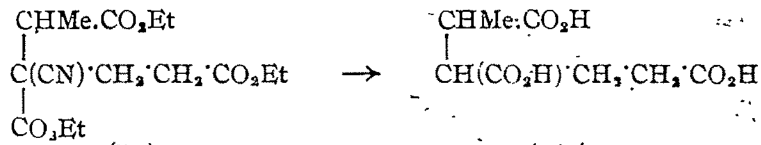

(III)

Palmen's quinone, m.p. 84-85°, can be prepared more conveniently by the oxidation of santenone with selenium dioxide in presence of acetic anhydride (*cf.* Simonsen, Evans and Ridgion, *J. Chem. Soc.*, 1934, 137). The quinone readily forms a beautifully crystalline quinoxaline derivative with *o*-phenylenediamine, m.p. 102-103°. As stated by Palmen (*loc. cit.*) the quinone forms a colourless hydrate, m.p. 138-40°, when left exposed to air or on treatment with alkali. The hydrate on heating, however, loses water and gives back the original quinone. A number of careful analyses have shown the quinone hydrate to possess the formula $C_9H_{12}O_2$, $\frac{1}{2}H_2O$. Obviously, further work will be necessary in order to elucidate the exact nature of the hydrate.

Santenonequinone on treatment with concentrated sulphuric acid (*vide* experimental) undergoes rearrangement with remarkable ease leading to the formation of a keto-acid,

$C_9H_{14}O_3$, m.p. 132°, which can be characterised by the formation of a semicarbazone, m.p. 192°. The keto-acid on oxidation with nitric acid gives a crystalline tricarboxylic acid, $C_8H_{12}O_6$, m.p. 181-82°, with the loss of a carbon atom. The tricarboxylic acid has been definitely shown to be identical with a specimen of pentane-βγε-tricarboxylic acid (V) prepared synthetically as follows :—

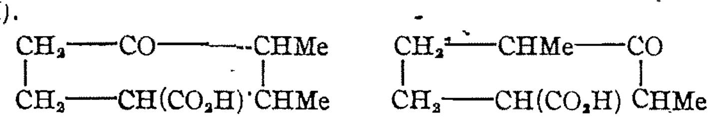
Ethyl α-cyano-β-methylsuccinate (Bone and Sprankling, *J. Chem. Soc.*, 1899, **75**, 853) interacts readily with ethyl β-chloropropionate, in presence of sodium ethoxide, forming ethyl γ-cyanopentane-βγε-tricarboxylate (IV).



(IV) (V)

When digested with sulphuric acid, the cyano-ester (IV) is hydrolysed with the elimination of carbon dioxide and formation of pentane-βγε-tricarboxylic acid, m.p. 182°, identical with the tricarboxylic acid derived from the oxidation of the keto-acid described above. The identity was further established by direct comparison and by the determination of mixed melting point.

It follows therefore that the original keto-acid can have either of the alternative structures (VI) and (VII).



(VI) (VII)

Of these, structure (VI) is to be preferred, since this alone is capable of being brought into satisfactory harmony with the general mechanism suggested, (Ingold *Chem. Soc.*, *Ann. Report*, 1927, p. 122) for the facile rearrangement of camphorquinone in presence of sulphuric acid. Final proof of the structure of the keto-acid, m.p. 132°, however, rests on the synthesis of an acid of structure (VI), which will form the subject matter of a later communication.

EXPERIMENTAL

Santenone used in these experiments was supplied by Messrs. Schimmel & Co., and was found to be optically inactive.

dl-*Santenonequinone* (I).—*dl*-Santenone (2·5 g.) was heated to 140°-150° in an oil-bath for 4 hours with acetic anhydride (3 c.c.) and selenium dioxide (3.2 g.). It was then filtered and the black residue of selenium washed with a little hot acetic acid. The solution was diluted with water, carefully neutralised with dilute sodium hydroxide solution, and extracted with ether. The solvent was then evaporated and the residue on distillation gave *dl*-santenonequinone (1.8 g.) as a mixture of solid and liquid. The liquid product was separated by treatment with a little petroleum ether and the residue purified by crystallisation from the same solvent when pure *dl*-santenonequinone was obtained in yellow crystals, m.p 84-85°. (Found : C, 70·5 ; H, 8·0. $C_9H_{12}O_2$ requires C, 71·0 ; H, 7·9 per cent).

The quinone, on keeping exposed to air, is slowly converted into a colourless crystalline *hydrate*, practically insoluble in petroleum ether. It crystallises from dilute acetic acid, m.p.

138-40°. This formation of the hydrate takes place readily in presence of dilute aqueous caustic soda. The hydrate loses water on heating and gives back the yellow quinone. (Found: C, 66·7 ; H, 8·2. $C_9H_{12}O_2$, $\frac{1}{2}H_2O$ requires C, 67·0 ; H, 8·0 per cent).

The quinone on heating with *o*-phenylenediamine in alcoholic or acetic acid solution gives the *quinoxaline* derivative which crystallises from dilute alcohol in colourless shining crystals, m.p. 102-103°. (Found : C, 79·8; H, 7·3. $C_{15}H_{16}N_2$ requires C, 80·3 ; H, 7·1 per cent.).

Rearrangement of dl-*Santenonequinone in presence of Concentrated Sulphuric Acid : Formation of* dl-2:3 *Dimethyl*cyclo*hexan-1-one-4-carboxylic Acid* (VI).—The finely powdered quinone (1 g.) was added gradually with shaking to concentrated sulphuric acid (9 c.c.) cooled in ice. The quinone went into solution with a yellow colour, which gradually dissappeared. It was kept in the cold for ½ hour and then poured on to powdered ice with stirring. The keto-acid was isolated by extraction with ether after saturating the solution with salt. To free it from neutral impurities, the ethereal solution was extracted with dilute sodium carbonate solution. The aqueous solution was acidified, saturated with salt and extracted with ether. The keto-acid (1g.) was obtained as a solid which crystallised from a mixture of benzene and petroleum ether, m.p. 132°. (Found : C, 63·3 ; H, 8·2. $C_9H_{14}O_3$ requires C, 63·5 ; H, 8·2 per cent).

The *semicarbazone* crystallised from spirit, m.p. 192°. (Found : C, 52·5 ; H, 7·4. $C_{10}H_{17}O_3N_3$ requires C, 52·8 ; H, 7·4 per cent).

Oxidation of the Keto-acid with Nitric Acid : Formation of Pentane-βγε-tricarboxylic Acid (V).—The keto-acid (1 g.) was heated carefully on a water-bath with concentrated nitric acid (15 c.c.) diluted with water (10 c.c.). After a few minutes a vigorous reaction started with copious evolution of nitrous gases. The heating was continued for about 1½ hours. The nitric acid was then evaporated off on the water-bath with frequent addition of water. The gummy product, thus obtained, was then triturated with a little concentrated hydrochloric acid and kept for sometime when a crystalline product was obtained. It was drained on a porous plate. The product (0·25 g.) was purified by crystallisation from concentrated hydrochloric acid, m.p. 181-82°. (Found : C, 46·7; H, 5·9. $C_8H_{12}O_6$ requires C, 47·0; H, 5·8 per cent).

Synthesis of Pentane-βγε-tricarboxylic Acid.

Ethyl γ-Cyanopentane-βγε-tricarboxylate (IV).—Ethyl α-cyano-β-methylsuccinate (7g.), prepared by condensing ethyl cyanoacetate with ethyl α-bromopropionate in presence of sodium ethylate according to Bone and Sprankling (*loc. cit.*), was added to an ice-cold solution of sodium (0·77 g.) in absolute alcohol (12·5 c.c.). Ethyl β-chloropropionate (5 g.) was then added to it drop by drop with shaking and kept overnight. The reaction was completed by refluxing on the water-bath for 5 hours. The product was diluted with water and extracted with ether. The extract was washed well with water, dried and the ether evaporated. The product remaining distilled at 168°/4 mm., yield 9 g. (Found : C, 57·2; H, 7·2 $C_{16}H_{23}O_6N$ requires C, 57·5 ; H, 7·3 per cent).

Pentane-βγε-tricarboxylic Acid (V).—The above product (8·5 g.) was heated on a sand-bath for 40 hours with water (8·5 c.c.) and concentrated sulphuric acid (8·5 c.c.). It was then diluted with water, saturated with salt and extracted repeatedly with ether. The solid residue obtained on evaporation of the solvent was crystallised from concentrated hydrochloric acid, m.p. 182° and found to be identical with the acid obtained by the oxidation of the keto-acid, $C_9H_{14}O_3$, which in its turn was obtained by the rearrangement of santenonequinone (no depression of mixed m.p.). (Found: C, 46·9; H, 5·9; Equiv., 67·85. $C_8H_{12}O_6$ requires C, 47·0; H, 5·8 per cent. Equiv,. 68·0.)

The *triethyl ester* was obtained by esterifying the acid by the alcohol-vapour method, b.p. 145°/4 mm. (Found: C, 57·9; H, 8·5. $C_{14}H_{24}O_6$ requires C, 58·3; H, 8·3 per cent).

The author takes this opportunity of expressing his indebtedness to Dr. J. C. Bardhan for his valuable help during the progress of this work.

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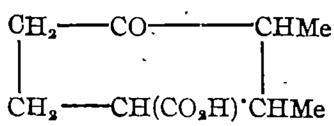
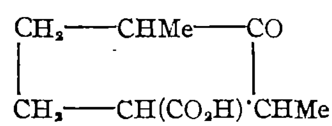
STUDIES IN THE CAMPHORQUINONE REARRANGEMENT. PART III. SYNTHESES OF 2:3-DIMETHYL*CYCLO*HEXAN-1-ONE-4-CARBOXYLIC ACID AND 3:6-DIMETHYL*CYCLO*HEXAN-1-ONE-4-CARBOXYLIC ACID

BY RAM NARAYAN CHAKRAVARTI

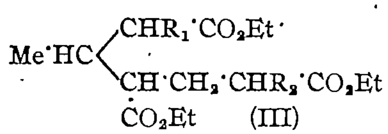
The ketonic acid, $C_9H_{14}O_3$, obtained by the rearrangement of santenonequinone in presence of sulphuric acid has now been definitely identified as 2:3-dimethyl*cyclo*hexan-1-one-4-carboxylic acid by direct synthesis of this acid, as well as the isomeric 3:6-dimethyl*cyclo*hexan-1-one-4-carboxylic acid by unambiguous methods. Incidentally it has been shown that the Dieckmann condensation of ethyl β-methylpentane-αγε-tricarboxylate leads to the formation of ethyl 3-methyl*cyclo*hexan-1-one-4:6-dicarboxylate and not the isomeric ester ethyl 3-methyl-*cyclo*hexan-1-one-2:4-dicarboxylate.

In a previous communication (*J. Indian Chem. Soc.*, 1944, **21**, 319) evidence was brought forward which appeared to show that the keto-acid, $C_9H_{14}O_3$, obtained by the action of sulphuric acid on santenonequinone, could be best represent d by the alternative structures (I) and (II). The most satisfactory way of deciding between these two formulæ seemed to be to prepare these acids synthetically and to compare the synthetical acids with the acid obtained from santenonequinone.


(I)


(II)

Ethyl crotonate has been condensed with ethyl sodio-cyanoacetate (*cf.* Hope and Perkin, *J. Chem. Soc.*, 1911, **99**, 762) and the resulting product on treatment with ethyl β-chloropropionate gives ethyl β-methyl-γ-cyanopentane-αγε-tricarboxylate (IV, R=H). This on hydrolysis and esterification furnishes the desired ester (III, $R_1=R_2=H$). Ethyl β-methylpentane-αγε-tricarboxylate on treatment with sodium gives a ketonic ester which can be represented by the alternative structures (V, $R_1=H$; $R_2=CO_2Et$; X=Et) and (V, $R_1=CO_2Et$; $R_2=H$; X=Et).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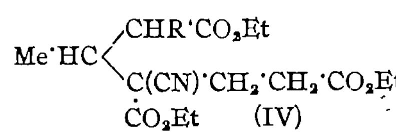
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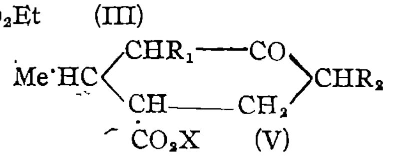
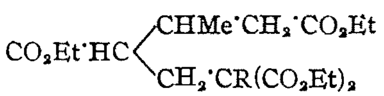

(V)

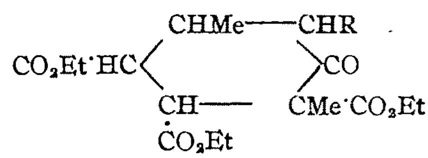
The product on hydrolysis furnishes 3-methyl*cyclo*hexan-1-one-4-carboxylic acid (V, $R_1=R_2=X=H$), m.p. 95-96° (semicarbazone, m.p. 208-209°).

The Dieckmann condensation product (V, $R_1=H$; $R_2=CO_2Et$; $X=Et$) or (V, $R_1=CO_2Et$; $R_2=H$; $X=Et$) on methylation, hydrolysis and esterification gives a tricarboxylic ester (III, $R_1=Me$; $R_2=H$) or (III, $R_1=H$; $R_2=Me$). This has been cyclised with sodium to give the keto-ester (V, $R_1=Me$; $R_2=CO_2Et$; $X=Et$) or (V, $R_1=CO_2Et$; $R_2=Me$; $X=Et$) and the latter on hydrolysis yields a keto-acid, m.p. 98-99° (semicarbazone, m.p. 216°) having the alternative structures (V, $R_1=Me$; $R_2=X=H$) or (V, $R_1=X=H$; $R_2=Me$). The keto-acids (V, $R_1=Me$; $R_2=X=H$) and (V, $R_1=X=H$; $R_2=Me$) have accordingly been synthesised by unambiguous methods in order to establish definitely the constitution of the keto-acid, m.p. 98-99°.

*The Synthesis of 3:6-Dimethyl*cyclo*hexan-1-one-4-carboxylic Acid* (V, $R_1=X=H$; $R_2=Me$).—Ethyl β-methylpentane-αγε-tricarboxylate (III, $R_1=R_2=H$) has been condensed with ethyl oxalate. The resulting product on distillation under reduced pressure gives ethyl-β-methylpentane-αγεε-tetracarboxylate (VI, $R=H$). This is methylated to give (VI, $R=Me$) and the latter on cyclisation with sodium furnishes the keto-ester (VII, $R=CO_2Et$) which on hydrolysis gives 3:6-dimethyl*cyclo*hexan-1-one-4-carboxylic acid (V, $R_1=X=H$; $R_2=Me$) (semicarbazone, m.p. 217°) identical with the product described above.



(VI)



(VII)

It is quite conceivable, however, that the tetracarboxylic ester (VI, $R=H$) may have an alternative structure (III, $R_1=CO_2Et$; $R_2=H$) and cannot, therefore, provide an adequate basis for the constitution of the keto-acid, m.p. 98-99°. 3 : 6-Dimethyl*cyclo*hexan-1-one-4-carboxylic acid has, therefore, been synthesised by an alternative route :

Ethyl 3-methyl*cyclo*hexan-1-one-4-carboxylate (V, $R_1=R_2=H$; $X=Et$) is condensed with ethyl oxalate and the resulting product on distillation furnishes ethyl 3-methyl*cyclo*hexan-1-one-4 : 6-dicarboxylate (V, $R_1=H$; $R_2=CO_2Et$; $X=Et$). This is methylated to give ethyl 3 : 6-dimethyl*cyclo*hexan-1-one-4 : 6-dicarboxylate (VII, $R=H$) and the latter on treatment with sodium ethylate yields ethyl βε-dimethylpentane-αγε-tricarboxylate (III, $R_1=H$; $R_2=Me$). This on cyclisation with sodium gives ethyl 3: 6-dimethyl*cyclo*hexan-1-one-2 : 4-dicarboxylate (V, $R_1=CO_2Et$; $R_2=Me$; $X=Et$) which could be smoothly hydrolysed to give 3 : 6-dimethyl*cyclo*hexan-1-one-4-carboxylic acid (V, $R_1=X=H$; $R_2=Me$), m.p. 98-99° (semicarbazone, m.p. 217°). It follows, therefore, that the sodium condensation of ethyl β-methylpentane-αγε-tricarboxylate (III, $R_1=R_2=H$) leads to the formation of ethyl 3-methyl*cyclo*hexan-1-one-4 : 6-dicarboxylate (V, $R_1=H$; $R_2=CO_2Et$; $X=Et$).

*The Synthesis of 2 : 3-Dimethyl*cyclo*hexan-1-one-4-carboxylic Acid* (V, $R_1=Me$; $R_2=X=H$).—Ethyl αβ-dimethylacrylate (*cf.* Frankland and Duppa, *Annalen*, 1900, **236**, 9; Wislicenus, *ibid.*, 1910, **272**, 9), prepared from the cyanohydrin of methyl ethyl ketone according to the method described in the experimental portion, has been condensed with ethyl sodio-

cyanoacetate and the resulting product allowed to react with ethyl β-chloropropionate to give ethyl $\alpha\beta$-dimethyl-γ-cyanopentane-$\alpha\gamma\epsilon$-tricarboxylate (IV, R=Me). The latter on hydrolysis yields

$$\mathrm{Me\,CH_2{\cdot}CO \rightarrow Me{\cdot}CH_2{\cdot}\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle CN}{\cdot}}{C}}{\cdot}OH \rightarrow Me{\cdot}CH : C(Me){\cdot}CN \rightarrow Me{\cdot}CH : C(Me){\cdot}CO_2Et}$$

(with Me over the first CO group as well: $\mathrm{Me\,CH_2{\cdot}\overset{\overset{Me}{|}}{C}O}$)

a liquid acid which is esterfied according to the alcohol-vapour method to give ethyl $\alpha\beta$-dimethylpentane-$\alpha\gamma\epsilon$-tricarboxylate (III, R_1=Me ; R_2=H). Sodium condensation then furnishes ethyl 2 : 3-dimethyl*cyclo*hexan-1-one-4 : 6-dicarboxylate (V, R_1=Me; R_2=CO_2Et ; X=Et) which on hydrolysis gives 2 : 3-dimethyl*cyclo*hexan-1-one-4-carboxylic acid (V, R_1=Me ; R_2=X=H), m.p. 132° (semicarbazone, m.p. 191°) which proves to be identical in every way with the keto-acid obtained from santenonequinone.

It follows, therefore, that the keto-acid, obtained by the rearrangement of santenonequinone must be best represented as 2 : 3-dimethyl*cyclo*hexan-1-one-4-carboxylic acid.

EXPERIMENTAL

Condensation of Ethyl Crotonate with Ethyl-Sodio-cyanoacetate and Ethyl β-Chloropropionate : Formation of Ethyl β-Methyl-γ-cyanopentane-αγε-tricarboxylate (IV, R=H).—Ethyl cyanoacetate (67·8 g.) was added to an ice-cold solution of sodium (13·8 g.) in absolute alcohol (225 c c.). Ethyl cortonate (68·4 g.) was then added to the curdy mass and the whole heated on a water-bath for 16 hours. The dark coloured solution was cooled in ice and ethyl β-chloropropionate (84 g.) added and kept overnight. It was then heated on the water-bath for 7 hours. The product was isolated by diluting the reaction mixture with water and extracting with ether. The extract was washed with water, and the ether evaporated. The *cyano-ester* (IV, R=H) was obtained as a colourless mobile liquid boiling at 195°/4 mm., yield 156 g. (Found : C, 58·7; H, 7·6. $C_{16}H_{25}O_6N$ requires C, 58·7 ; H, 7·6 per cent).

Ethyl β-Methylpentane-αγε-tricarboxylate (III, R_1=R_2=H).—The above condensation product (156 g.) was hydrolysed by heating on a sand-bath for 40 hours with concentrated sulphuric acid (175 c.c.) diluted with water (210 c.c.). It was then diluted with water, saturated with salt and extracted with ether. The crude tricarboxylic acid (85 g.) was obtained as a viscous liquid on evaporation of the ether. It was heated to 110° with absolute alcohol (170 c.c.) and concentrated sulphuric acid (17 c.c.) and esterified in a current of alcohol vapour for 6 hours. The product was worked up in the usual manner and distilled. The pure tricarboxylic ester (III, R_1=R_2=H) boils at 168°/6 mm., yield 93 g. (Found : C, 59·3; H, 8·6; $C_{15}H_{26}O_6$ requires C, 59·6; H, 8·6 per cent).

Sodium Condensation of Ethyl β-Methylpentane-αγε-tricarboxylate : Formation of (V, R_1=CO_2Et; R_2=H; X=Et) or (V, R_1=H ; R_2=CO_2Et ; X=Et).—The triethyl ester (30.2g.), obtained above, was heated on the water-bath with finely divided sodium (3.4 g.) and dry benzene (70 c.c.). The reaction started after about 45 minutes and was complete in 2 hours more. It was then cooled, treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated and washed well with water. The oil obtained after removal of the benzene, was distilled in *vacuo*, when practically the whole of it distilled over at 158°/6mm., yield 22·5 g. It gave a violet colouration with alcoholic ferric chloride. (Found : C, 60·4; H, 7·7. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8 per cent).

*Hydrolysis of the Above Sodium Condensation Product : Formation of 3-Methyl*cyclo*hexan-1-one-4-carboxylic Acid* (V, $R_1=R_2=X=H$).—The β-ketonic ester (22 g.), obtained above, was refluxed on the sand-bath for 6 hours with 10 volumes of 6% hydrochloric acid. The clear solution thus obtained was cooled, neutralised with soda and extracted with ether to remove any neutral matter. The aqueous solution was acidified, saturated with salt and extracted repeatedly with ether. On evaporation of the solvent the keto-acid(V, $R_1=R_2=X=H$) (11 g.) was obtained as a liquid, which solidified in a vacuum desiccator.

The *semicarbazone* crystallises from spirit and melts with decomposition at 208-209°. (Found : C, 50.5; H, 6.9. $C_9H_{15}O_3N_3$ requires C, 50.7; H, 7.0 per cent).

The *pure* keto-acid was prepared by hydrolysing the semicarbazone with dilute hydrochloric acid. It crystallises from a mixture of benzene and petroleum ether, m p. 95-96°. (Found : C, 61.6 ; H, 7.6. $C_8H_{12}O_3$ requires C, 61.5 ; H, 7.7 per cent).

The *ethyl ester* was prepared by heating the crude keto acid (8 g.) for 10 hours on the water-bath with absolute alcohol (30 c.c.) and 5 c c. of alcoholic hydrogen chloride (saturated at 0°). The alcohol was then distilled off and the liquid remaining in the flask was diluted with water and extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution and water. *Ethyl 3-methyl*cyclo*hexan-1-one-4-carboxylate* was obtained as a light colourless liquid boiling at 112°/5mm., yield 7 g. (Found: C, 65.0 ; H, 8.6. $C_{10}H_{16}O_3$ requires C, 65.2; H, 8.7 per cent).

The *semicarbazone* of the ethyl ester crystallises from dilute alcohol, m.p. 136°. (Found: C, 54.6; H, 7.9. $C_{11}H_{19}O_3N_3$ requires C, 54.7; H, 7.9 per cent).

Methylation of the Sodium Condensation Product of Ethyl β-methylpentane-$\alpha\gamma\epsilon$-tricarboxylate.—For this purpose the sodiosalt, obtained by heating the triethyl ester (III, $R_1=R_2=H$) (30.2g.), with finely divided sodium (4.6g.) in benzene (75 c.c.) was cooled in ice and treated with methyl iodide (13 c.c.) and kept overnight. It was then heated on the water-bath for 8-10 hours with the addition of a little methyl iodide from time to time. When cold it was treated with water, the benzene layer separated, washed with water, and the benzene evaporated. The methylated product boiled at 160°/7mm., yield 24 g. It gave no colouration with alcoholic ferric chloride. (Found : C. 61.8; H, 8.3. $C_{14}H_{22}O_5$ requires C, 62.2; H, 8.15 per cent).

Acid Hydrolysis of the above Methylated Product and its subsequent Esterification : Formation of (III, $R_1=Me$; $R_2=H$) or (III, $R_1=H$; $R_2=Me$).—The methylated product (18g.) obtained above was heated on the water-bath for 3 hours with excess of 20% alcoholic potash. The alcohol was then evaporated off with the addition of water. The aqueous alkaline solution was acidified, saturated with salt and extracted with ether. The gummy residue (14.3g.), obtained on evaporation of the solvent, was esterified by the alcohol-vapour method. The triethyl ester (III, $R_1=Me$; $R_2=H$) or (III, $R_1=H$; $R_2=Me$) was obtained as a colourless oil boiling at 160°/5mm., yield 13.9 g. (Found: C, 60.3: H, 8.6. $C_{16}H_{28}O_6$ requires C, 60.7; H, 8.8 per cent).

Sodium Condensation of the above Triethyl Ester : Formation of (V, $R_1=Me$: $R_2=CO_2Et$; $X=Et$) or (V, $R_1=CO_2Et$; $R_2=Me$; $X=Et$).—The triethyl ester, obtained in the preceeding experiment, was heated on the water-bath with finely divided sodium (1.8 g) suspended in dry benzene (34. c.c.). A vigorous evolution of hydrogen started after half an hour and in another two hours the whole of the sodium went into solution. The brown liquid was cooled in ice, treated with ice-water and acidified with ice-cold dilute hydrochloric acid.

The upper benzene layer was separated, and washed with water. The product obtained on distillation of the solvent boiled constantly at 154°/5mm., yield 6 g. It gave a strong colouration with alcoholic ferric chloride. (Found : C, 61·9; H, 8·0. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1 per cent).

Ketonic Hydrolysis of the above Product: Formation of the Keto-acid, m.p. 98-99°.—The β-ketonic ester (5.7g.), obtained above, was heated on a sand-bath for 6-7 hours with 60 c.c. of 6% hydrochloric acid. It was then neutralised with soda and extracted with ether to remove any neutral matter. The alkaline solution was acidified, saturated with salt and extracted with ether. The crude keto-acid, thus obtained, was converted into the *semicarbazone*. After crystallisation from spirit it melted at 216° with decomposition. (Found: C, 52·6; H, 7·3. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·4 per cent).

The *pure* keto-acid was obtained by hydrolysing the semicarbazone with dilute hydrochloric acid. It was obtained as a colourless viscous liquid, b.p. 155°/4mm. It solidified completely on keeping for several days. The solid acid crystallises from a mixture of benzene and petroleum ether, m.p. 98-99°. (Found: C, 63·3; H, 8·1. $C_9H_{14}O_3$ requires C, 63·5; H, 8.2 per cent).

*Synthesis of 3:6-Dimethyl*cyclo*hexan-1-one-4-carboxylic Acid* (V, R_1=H; R_2=Me;X=H).

Ethyl β-Methylpentane-αγεε-tetracarboxylate (VI, R=H).—Absolute alcohol (2·96 g.), distilled over calcium, dissolved in dry ether (6 c.c.) was added dropwise to a suspension of finely divided potassium (2·5 g.) in dry ether (65 c.c.) cooled in ice-water. It was then kept at the room temperature till the whole of the potassium disappeared. It was again cooled in ice and diethyl oxalate (9·4 g.) was added slowly. Ethyl β-methylpentane-αγε-tricarboxylate (19·4 g.) was then added dropwise to the cold solution. It was kept for 24 hours and then diluted with ice-water. The ethereal layer was separated and the aqueous layer extracted once with ether. The aqueous alkaline solution was then acidified with ice-cold dilute sulphuric acid and extracted with ether. The extract was washed well with water and the ether evaporated. The residual oil was heated to 110-120° in *vacuo* for about an hour and then heated under atmospheric pressure for about 24 hours, till it gave no colouration with alcoholic ferric chloride, the temperature being gradually raised from 160° to 190° during this period. It was finally distilled in *vacuo*, b.p. 175°/5mm., yield 13·8 g. (Found: C. 57·3; H, 7·8. $C_{18}H_{30}O_8$ requires C, 57·7 ; H, 8·0 per cent).

Ethyl-βε-Dimethylpentane-αγεε-tetracarboxylate (VI, R=Me).—The above tetraethyl ester (13·5 g.) was added to molecular sodium (0·84 g.) suspended in dry benzene (35 c.c.), cooled in ice, and kept overnight. It was again cooled in ice and methyl iodide (5 c.c.) was added and again kept overnight. The methylation was completed by heating on the water-bath for 8 hours with the addition of a little methyl iodide from time to time. When cold it was treated with water, the benzene layer was separated, washed, dried and the benzene evaporated. The liquid remaining was then distilled in *vacuo*, b.p. 180°/6 mm , yield 11·4 g. (Found : C, 58·5; H, 8·2. $C_{19}H_{32}O_8$ requires C, 58·7 ; H, 8·2 per cent).

*Ethyl 3 : 6-Dimethyl*cyclo*hexan-1-one-2 : 4 : 6-tricarboxylate* (VII, R=CO_2Et).—The methylated tetracarboxylic ester (11·2 g.) was heated on the water-bath with a fine suspension of sodium (1·08 g.) in benzene (25 c.c.). After about 3 hours the sodium completely went into solution. The liquid was treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed well with water and the benzene evaporated,

The residual liquid was then distilled in *vacuo*, b.p. 170°/6mm., yield 8·7 g. (Found: C, 59·8; H, 7·4. $C_{17}H_{26}O_7$ requires C. 59·6; H, 7·6 per cent).

*Weak Hydrolysis of the above Product: Formation of 3:6-Dimethyl*cyclo*hexan-1-one-4-carboxylic Acid* (V, R_1=X=H; R_2=Me).—The ketonic ester, obtained above (8·5 g.), was heated on a sand-bath for about 10 hours with 100 c.c. of 10% sulphuric acid The solution was made alkaline with sodium carbonate and extracted with ether to remove any neutral matter present. The aqueous solution was then acidified, saturated with salt and extracted with ether. The light brown liquid residue, obtained after evaporation of the solvent, was converted into the *semicarbazone*, which after cystallisation from spirit melted at 217° with decomposition and was found to be identical with the semicarbazone of the keto-acid, m.p. 98-99°, previously described. (Found: C, 52·6; H, 7·4. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·4 per cent).

*Condensation of Ethyl 3-Methyl*cyclo*hexan-1-one-4-carboxylate* (V, R_1=R_2=H; X=Et) *with Ethyl oxalate; Formation of pure Ethyl 3-methyl*cyclo*hexan-1-one-4:6-dicarboxylate* (V, R_1=H; R_2=CO_2Et; X=Et).—A mixture of ethyl 3-methyl*cyclo*hexan-1-one-4-carboxylate (23 g.) and ethyl oxalate (18·3 g.) was added slowly with shaking to a solution of sodium (2·88 g.) in absolute alcohol (37·5 c.c.) kept cooled in a freezing mixture and the solution kept overnight. The product was treated with ice-water and extracted with ether to remove any unreacted ester present. The aqueous solution was then acidified with ice-cold dilute sulphuric acid, extracted with ether and the extract washed well with water. The oily liquid, obtained after removal of the solvent, was heated at 110-120° under reduced pressure for an hour and then heated under atmospheric pressure for about 3 hours till the evolution of carbon monoxide ceased completely. The temperature of the bath during this period was raised gradually from 170-90°. It was finally distilled under diminished pressure when ethyl 3-methyl*cyclo*hexan-1-one-4:6-dicarboxylate (V, R_1=H; R_2=CO_2Et; X=Et) (12·8 g.), unmixed with the isomeric ester (V, R_1=CO_2Et; R_2=H; X=Et), was obtained boiling at 155°/6 mm. It gave a violet colouration with alcoholic ferric chloride.

*Ethyl 3:6-Dimethyl*cyclo*hexan-1-one-4:6-dicarboxylate* (VII, R=H).—The above ester (12·8 g.) was added to molecular sodium (1·15 g) suspended in dry benzene (25 c.c.), cooled in ice and kept overnight. Methyl iodide (6 c c.) was added to the ice-cold sodio-salt and it was again kept overnight. The methylation was completed by heating on the water-bath for 8 hours with the addition of a little methyl iodide from time to time. The product was treated with water. The benzene layer was separated, washed with cold 15 per cent caustic potash solution to remove any trace of unmethylated ester, and finally with water. The product was then distilled. Ethyl 3:6-dimethyl*cyclo*hexan-1-one-4:6-dicarboxylate was obtained as a colourless mobile liquid, b.p. 158°/6 mm., yield 11·8 g. It gave no colouration with ferric chloride. (Found: C, 61·7; H, 8·2. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1 per cent).

Ethyl βε-Dimethylpentane-αγε-tricarboxylate (III, R_1=H; R_2=Me).—The methylated product (11·6 g.), obtained above, was heated on the water-bath for 4 hours with a solution of sodium (0·25 g.) in absolute alcohol (11 c.c.). It was then cooled, diluted with water, acidified with hydrochloric acid and extracted with ether. The product obtained on removal of the ether was distilled in *vacuo*. Ethyl βε-dimethylpentane-αγε-tricarboxylate boils at 163°/6 mm., yield 11·5 g.

*Ethyl 3:6-Dimethyl*cyclo*hexan-1-one-2:4-dicarboxylate* (V, R_1=CO_2Et; R_2=Me; X=Et) was prepared by heating the above trimethyl ester (11·5 g.) on the water-bath with a suspension of finely divided sodium (1·15 g.) in dry benzene (27 c.c.). A vigorous reaction started on heating and it was complete in an hour and a half. The product was

cooled, treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The upper benzene layer was separated, washed with water and the benzene was then evaporated. The residue on distillation under diminished pressure gave a colourless mobile liquid, b.p. 150°/6 mm., yield 8·2 g. It gave a colouration with ferric chloride. (Found: C, 62·0; H, 8·0. $C_{14}H_{22}O_5$ requires C, 62·2; H. 8·1 per cent).

3:6-*Dimethyl*cyclo*hexan-1-one-4-carboxylic Acid* (V, R_1=X=H; R_2=Me) was obtained from the above ester (8 g.) by heating on a sand-bath with 6 % hydrochloric acid (80 c.c.). After about 8 hours an almost clear solution was obtained. It was then cooled, neutralised with sodium carbonate and extracted with ether to remove any neutral matter. The aqueous solution was acidified, saturated with salt and extracted repeatedly with ether. The keto-acid (4·5 g.) was obtained as a light brown liquid on evaporation of the solvent.

The *semicarbazone* crystallises from spirit as a sandy white powder which melts with decomposition at 217°, and is identical with the semicarbazone of the keto-acid, m.p. 98-99° as described previously (mixed m.p.). (Found: C, 52·5; H, 7·3. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·4 per cent).

The *pure* keto-acid was obtained by hydrolysing the semicarbazone with hydrochloric acid (1:1). It crystallises from a mixture of benzene and petroleum ether, m.p. 98-99°, and is identical with the keto-acid, m.p. 98-99°, as obtained previously (mixed m.p.). (Found: C, 63·3; H, 8·1. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2 per cent).

*Synthesis of 2:3-Dimethy*cyclo*hexan-1-one-4-carboxylic Acid* (V, R_1=Me, R_2=X=H).

Methyl ethyl ketone cyanohydrin.—Pure methyl ethyl ketone (84 c.c.) was added dropwise, during the course of one hour and a quarter, to a solution of sodium cyanide in water (90 c.c.), cooled in ice and stirred mechanically. Sulphuric acid (40%, 68 c.c.) was then added to it in 3 hours and the stirring (7·5 g.) was continued for another half hour. The liquid was then filtered at the pump and the salts washed with ether. The filtrate was extracted with ether The total ethereal extract was dried over anhydrous calcium chloride and the solvent evaporated after adding a drop of sulphuric acid. The residual oil on distillation gave the cyanohydrin boiling at 130°/60 mm., yield 56 g.

Ethyl αβ-Dimethylacrylate.—Methyl ethyl ketone cyanohydrin (72 g.), dry ether (215 c.c.) and dry pyridine (200 c.c.) were taken in a litre three-necked flask provided with a mercury-sealed stirrer, a dropping funnel and a reflux condenser. The contents were cooled in ice and stirred vigorously while thionyl chloride (80 c.c.) was added through the dropping funnel during 3 hours. The stirring was continued for 15 minutes after the addition was complete. The flask was then heated to 50° for 3 hours. During this time the reaction mixture was stirred occasionally. The product was finally decomposed with powdered ice and the ethereal layer separated. The aqueous portion was extracted several times with ether. The ether solution was washed with dilute hydrochloric acid, then with dilute caustic soda solution and finally with water. It was then dried over anhydrous calcium chloride and the solvent evaporated. The residual liquid on distillation gave the unsaturated nitrile (45·5 g.) boiling at 90°/60 mm.

The unsaturated nitrile, thus obtained, was heated in an oil-bath at 140-150° for 20 hours with absolute alcohol (75 c.c.), rectified spirit (75 c.c.) and concentrated sulphuric acid (64 c.c.). It was then diluted with water and extracted several times with ether. The ethereal extract was washed with dilute sodium carbonate solution and water. It was then dried over anhydrous calcium chloride and fractionated when ethyl αβ-dimethylacrylate was obtained as a

colourless liquid with a characteristic odour boiling at 140°-145°, yield, 32·5 g. Some unesterified acid can be recovered from the sodium carbonate extract.

Ethyl αβ-Dimethyl-γ-cyanopentane-αγε-tricarboxylate (IV, R=Me).—Ethyl cyanoacetate (22·6 g.) was added to an ice-cold solution of sodium (4·6 g.) in absolute alcohol (75 c.c.). Ethyl αβ-dimethylacrylate (25·6 g.) was then added and it was refluxed on the water-bath for 14 hours. The dark coloured solution was cooled in ice and ethyl β-chloropropionate (27·4 g.) was added drop by drop, and kept overnight. The reaction was completed by heating on the water-bath for 6 hours. When cold it was diluted with ether. The ethereal solution was washed, dried and the ether evaporated. The *cyanoester* (IV, R=Me) was obtained as a colourless oil boiling at 200°-204°/6mm., yield 46 g. (Found: C, 60·3; H, 7·8. $C_{17}H_{27}O_6N$ requires C, 59·8; H, 7·9 per cent).

Ethyl αβ-Dimethylpentane-αγε-tricarboxylate (III, R_1=Me; R_2=H).—The above cyanoester (45 g.) was dissolved in concentrated sulphuric acid (52 c.c.) and then diluted with water (63 c.c.). It was heated on a sand-bath for 40 hours and then diluted with water, saturated with salt and extracted with ether. The residue (30 g.), obtained on evaporation of the ether, was esterified by the alcohol-vapour method. *Ethyl αβ-dimethylpentane-αγε-tricarboxylate* was obtained as a colourless mobile liquid boiling at 178°/7 mm., yield 29 g. (Found: C, 60·5; H, 8·7. $C_{16}H_{28}O_6$ requires C, 60·7; H, 8·8 per cent).

*Ethyl 2:3-Dimethyl*cyclo*hexan-1-one-4:6-dicarboxylate* (V, R_1=Me; R_2=CO_2Et; X=Et).—The triethyl ester (27·6 g.), obtained above, was heated on the water-bath with a fine suspension of sodium (3·7 g.) in dry benzene (66 c.c.). After an hour's heating a vigorous evolution of hydrogen started when the flask was removed from the water-bath. The reaction was finally completed by heating for 2 hours more. When cold the product was treated with ice-water and acidified with ice-cold dilute hydrochloric acid. The benzene layer was separated, washed and the benzene evaporated. The oil was then distilled under reduced pressure when it was obtained as a colourless oil, b. p. 170°/8 mm., yield 20 g. It gave a strong ferric reaction. (Found: C, 61·9; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1 per cent).

*2:3-Dimethyl*cyclo*hexan-1-one-4-carboxylic acid* (V, R_1=Me; R_2=X=H) was prepared by hydrolysing the above β-ketonic ester (19 g.) with concentrated hydrochloric acid (37 c.c.) diluted with water (106 c.c.). The mixture was heated on the sand-bath for 6 hours, cooled, saturated with salt and extracted with ether. The residue, obtained on evaporation of the ether, was heated on the water-bath for an hour with caustic potash (8 g.) in 10 per cent aqueous alcoholic solution. It was worked up in the usual way and the crude keto-acid (11·5 g.) obtained was converted into the *semicarbazone*. It crystallises from water as a sandy white powder melting with decomposition at 191° and identical with the semicarbazone of the keto-acid by the rearangement of santenonequinone (mixed m. p.). (Found: C, 52·6; H, 7·4. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·4 per cent).

The *pure* keto-acid was obtained by the hydrolysis of the semicarbazone with 10% hydrochloric acid. It crystallises from a mixture of benzene and petroleum ether, m. p. 132° and is identical with the keto-acid, obtained by the rearrangement of santenonequinone (mixed m. p.). (Found: C, 63·4; H, 8·2. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2 per cent).

The *ethyl ester* of the above keto-acid (2·5 g.) was prepared by heating it with 2 c.c. of alcoholic hydrogen chloride (saturated at 0°) and absolute alcohol (20 c.c.) and working up in the usual manner. In was obtained as a colourless liquid, b.p. 110°/5mm., yield 2·5 g. (Found: C, 66·5; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·09 per cent).

The *semicarbazone* of the ethyl ester crystallises from dilute alcohol in colourless shining laminae, melting at 187° with decomposition. (Found: C, 56·1; H, 8·1. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·2 per cent).

The author's grateful thanks are due to Dr. J. C. Bardhan for his kind advice and criticism.

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STUDIES ON SOME BINARY SYSTEMS OF ORGANIC COMPOUNDS

By R. K. Barua

The refractive index-composition curves of certain acid-ketone and acid-ester systems have been investigated. The following are the systems studied:—(a) acid-ketone system:—(i) trichloro-acetic acid-acetone; (ii) acetic acid-acetophenone; (iii) propionic acid-acetone; (iv) n-butyric acid-acetone; (b) acid-ester system:—(i) trichloroacetic acid-ethyl benzoate; (ii) acetic acid-ethyl benzoate, (iii) acetic acid—ethyl acetate.

It has been found that in the above cases, except system (a, ii) the refractive index-composition curves are distinctly concave to the concentration axis, thus suggesting the formation of intermediate complexes

The refractive index-composition curves of binary liquid mixtures have been studied by various investigators (Pushin and Matavulj, *Z. physikal. Chem.*, 1933, **161**, 341; **162**, 415; Burnham and Madgin, *J. Chem. Soc.*, 1936, 789; Ansov, *Ann. Inst. Physico-chim, Leningrad*, 1926, **3**, 379, 455; Rao and Narayanaswamy, *Proc. Indian Acad. Sci.*, **9A**, 35).

According to Pushin and Matavulj, in systems where compound formation takes place, the refractivity curve shows positive deviations from the mixture law. In another investigation, Kendall and Brakeley (*J. Amer. Chem. Soc.*, 1921, **43**, 1826) have shown with viscosity measurements, extensive compound formation in certain acid-ketone, acid-ester systems. Similar studies have been undertaken in the present investigation, with a view to typifying some of the binary systems from the variations of refractive indices with the composition.

Experimental

The starting materials were Merck's extra pure reagents. They were further purified by repeated distillation. The variations in refractive index with composition have been shown in the succeeding tables. Pulfrich refractometer was used and sodium light employed. The refractive index for trichloroacetic acid has been calculated from its value of molecular refractivity.

Table I

Trichloroacetic acid: ethyl benzoate (at 20°)

Mol. % of the acid.	Refractive Index.
0	1·5059
7	1·5044
22	1·5026
32·6	1·5006
46·9	1·4974
65	1·4926
73·6	1·4887
82·4	1·4832
100	1·4727

Table II

Acetic acid: ethyl benzoate (at 18°)

Mol. % of the acid.	Refractive Index.
0	1·5059
12·03	1·4917
24·5	1·4764
38·8	1·4558
47·9	1·4463
53·6	1·4377
71·5	1·4131
83	1·3982
100	1·3719

Table III

Acetic acid: ethyl acetate (at 18°)

Mol. % of the acid.	Refractive Index.
0	1·3702
6·4	1·3710
16·3	1·3723
17·7	1·3725
29·9	1·3730
39·2	1·3731
46·1	1·3732
53·2	1·3731
63·9	1·3731
77·1	1·3728
100	1·3719

TABLE IV

Trichloroacetic acid : acetone (at 20°)

Mol. % of acid.	Refractive Index.
0	1·3588
10	1·3822
15	1·3922
18	1·3973
30	1·4158
37	1·4243
52	1·4410
69	1·4563
80	1·4634
100	1·4727

TABLE V

Propionic acid : acetone (at 19·5°)

Mol. % of acid.	Refractive Index.
0	1·3588
23	1·3678
33	1·3710
42·5	1·3740
49·9	1·3759
66	1·3802
74·5	1·3820
79·9	1·3831
92	1·3850
100	1·3865

TABLE VI

n-Butyric acid : acetone (at 17·5°)

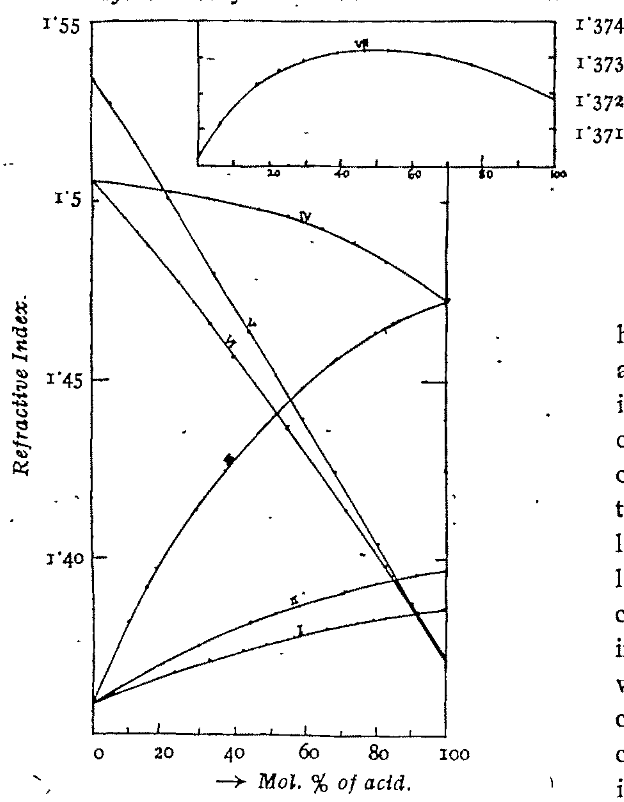
Mol. % of acid.	Refractive Index.
0	1·3588
20	1·3700
29·9	1·3754
43·9	1·3822
51	1·3842
70·2	1·3908
80	1·3926
91	1·3955
100	1·3979

TABLE VII

Acetic acid : acetophenone (at 22°)

Mol % of acid.	Refractive Index.
0	1·5342
5·3	1·5279
12·06	1·5170
20·6	1·4994
34·1	1·4801
43·7	1·4634
51·5	1·4513
58·7	1·4393
68·8	1·4240
81	1·4042
100	1·3719

Fig. 1 shows the graphs obtained by plotting the refractive indices against the concentrations of one of the components of the binary mixtures. The inset in Fig. 1 shows the curve for the system ethyl acetate: acetic acid. In calculating the molar percentages, acetic acid



Curve I—Propionic acid—acetone
Curve II—*n*-butyric—acetone
Curve III—CCl_3COOH—acetone
Curve IV—CCl_3COOH—ethyl benzoate
Curve V—acetic acid—acetophenone
Curve VI—acetic acid—ethyl benzoate
Curve VII—acetic acid—ethyl acetate

has been taken to be dimeric since this is an associated liquid. In the cases studied it has been found that all the curves except curve V are markedly concave to the concentration axis. This points out that these systems do not obey the mixture law. These deviations from the mixture law leads to the inference that in these cases there is most probably formation of intermediate complexes. Such inferences were also drawn from a study of similar curves by Ansov (*loc. cit.*) who holds that curves concave to the concentration axis indicate reciprocal chemical action.

My thanks are due to Prof. J. L. Mukherjee, M.Sc., for his kind encouragement and help. I am also indebted to Prof. S. C. Chatterjee for the facilities he has given me for carrying out this piece of work.

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STUDIES IN THE SANTALOL SERIES. PART IV. CHEMISTRY OF GUERBET'S SANTALIC ACID

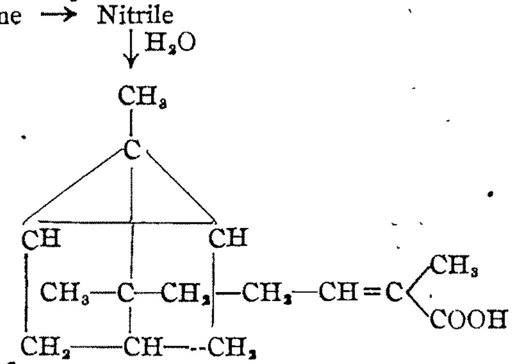
By P. C. Guha and S. C. Bhattacharyya

Guerbet's santalic acid has been isolated from sandalwood oil and its properties thoroughly compared with those of α-santalic acid (prepared from α-santalol), from which it has been found to differ fundamentally. Both chemical and spectroscopic evidences indicate that the substance is probably a saturated tetracyclic sesquiterpene derivative, and hence different from both α- and β- santalic acids. The substance has now been named γ-santalic acid, only because of its occurrence in sandalwood oil.

Among the different constituents of sandalwood oil, the acidic substance first isolated by Guerbet (*Comp. rend.*, 1900, **130**, 417) and named by him as santalic acid behaves rather peculiarly. From his results of analysis, he ascribed the formula $C_{15}H_{24}O_2$ to the substance and without advancing any other experimental évidences named the substance as above, meaning thereby that the substance was the corresponding carboxylic acid of santalol. At the time of Guerbet, very little information was known about the chemistry of α-santalol and anything obtained from sandalwood oil was expected in some way or other to be related with the former. From our investigations it has now been found that Guerbet's acid is a tetracyclic saturated compound having no structural relationship with α-santalol, and hence the name santalic acid suggested by Guerbet for this acid evidently on the assumption that it is derived from santalol, does not seem to be correct.

Later, Semmler (*Ber.*, 1907, **40**, 1120, 1124) oxidised α-santalol to α-santalal and subsequently converted it into the corresponding carboxylic acid and correctly named it santalic acid, although the name α-santalic acid would have been more appropriate.

$$\alpha\text{-Santalol} \xrightarrow{CrO_3} \alpha\text{-Santalal} \xrightarrow{NH_2OH} \text{Oxime} \xrightarrow{-H_2O} \text{Nitrile}$$



α-Santalic acid

The properties of Semmler's α-santalic acid, prepared from santalol, do not seem to have been compared by him with those of Guerbet's natural santalic acid. Semmler's paper (*loc. cit.*) was published about seven years later than that of Guerbet (*loc. cit.*), but as Semmler named his substance also as santalic acid, it seems probable that he considered his acid to be identical with that of Guerbet, evidently because these two acids were known to possess nearly identical boiling points and percentage composition.

For a closer and detailed examination a small amount of Guerbet's acid has now been isolated from sandalwood oil, and its properties compared with those of Semmler's α-santalic acid. The data as given below are evidently not identical and rather anomalous.

—	α-Santalic acid	Guerbet's acid
1. Mol. formula	$C_{15}H_{22}O_2$	$C_{15}H_{22}O_2$
2. Equivalent weight	234·326	235·3

	α-Santalic acid.	Guerbet's acid
3. Action of pot. permanganate	decolourises	decolourises
4. Unsaturation value (percamphoric acid)	*one double bond*	*0·2 to 0·4 double bond*
5. Spectroscopic evidence	—	*mostly saturated*
6. Boiling point	193°/9mm.	189°/9 mm.
7. n_D^{20} of the acid	1·5055	1·5057
8. B.p. of methyl ester	146°/9 mm.	141°/9 mm.
9. n_D^{20} of methyl ester	1·4910	1·4914
10. d_4^{20} of methyl ester	1·0021	1·02858

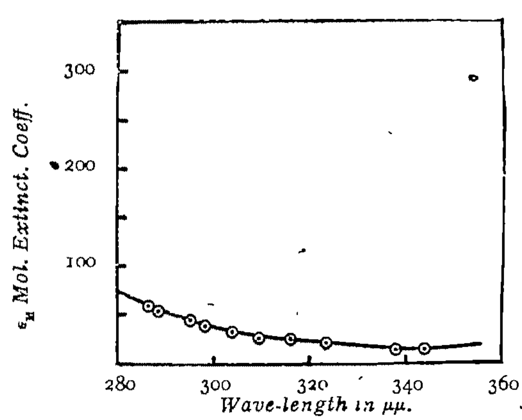
Although the equivalent weight, percentage composition, boiling points and particularly the refractive indices of the acids and their methyl esters are quite close, the densities and the unsaturation numbers of the methyl esters of the two acids are so wide apart that they can never be regarded as identical and there must be some fundamental difference between the two acids.

Critical examination of density.—It is a general rule that in any series of acids belonging to the same family, densities of the methyl esters decrease with the increasing molecular weights. Densities of the methyl esters of the different acids of the α-santalol series are given below:

Name of ester.	Density, d_4^{20}
1. Methyl teresantalate ($C_{11}H_{16}O_2$)	1·0320
2. Methyl nor-tri*cyclo*ekasantalate ($C_{12}H_{18}O_2$)	1·0230
3. Methyl tri*cyclo*ekasantalate ($C_{13}H_{20}O_2$)	1·0164
4. Methyl α-santalate ($C_{16}H_{24}O_2$)	1·0020

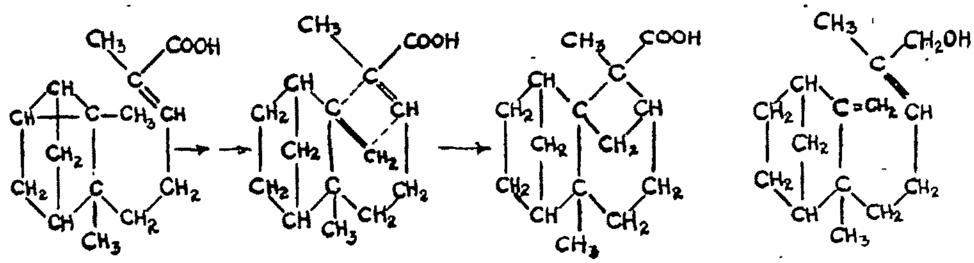
It is clear from the above table that all the esters of the acids of the α-santalol series, including the methyl ester of α-santalic acid itself obey this generalisation; but the methyl ester of Guerbet's acid ($C_{16}H_{24}O_2$) possesses a density of 1·02858. Therefore, it cannot belong to the compounds of the α-series. Neither can it belong to the β-series, the members of which possess an additional double bond and consequently should possess even lower densities.

Spectroscopic Evidence and Unsaturation Number.—Determination of the unsaturation number of Guerbet's acid with percamphoric acid reveals that its unsaturation number lies between 0·2 to 0·4. This is a positive indication that it is a mixture of some saturated and unsaturated compounds. From the examination of the absorption spectra of the substance in the ultraviolet region, it is found to give a flat absorption curve (*vide curve*) like that of acetic acid. From these results the only reasonable conclusion can be that Guerbet's acid is a saturated compound mixed with some unsaturated compounds as impurities.



It will be shown in part V of this series that Guerbet's acid is accompanied in nature by a considerable amount of β-santalic acid, which has been isolated by the authors for the first time. The new substance possesses two double bonds and is a highly refractive liquid. The unsaturation number of 0·2 to 0·4 shown by Guerbet's acid may, therefore, be due to the presence of a small quantity of β-santalic acid, the complete separation of which from the former by the usual process of fractional distillation is extremeley difficult.

Constitution.—It is possible that Guerbet's acid is probably formed in nature from α-santalic acid (perhaps formed from α-santalol by some natural process of oxidation) through some rearrangement and may possibly be a tetracyclic compound of the type shown below.



α-Santalic acid (camphene type) — Intermediate phase (β-type) — Guerbet's acid — β-Santalol (camphene type)

Thus according to the above postulation, it possesses a formula $C_{15}H_{22}O_2$ and is a tetracyclic isomer of α-santalic acid. That this type of rearrangement of α-santalic acid is not impossible is suggested from the exocyclic ethylenic structure of β-santalol advanced by Ruzicka and co-workers (*Helv. Chim. Acta.*, 1935, **18**, 355), as shown above.

The following facts are also in favour of the above tetracyclic saturated structure:

1. The compound possesses four fused rings and is saturated, consequently its methyl ester should possess a higher density than that of α-santalic acid and this is actually so.

2. The substance possesses a formula $C_{15}H_{22}O_2$ and is saturated. Therefore, taking the validity of the isoprone theory about terpenes, it should have a tetracyclic structure.

3. The acid does not form an anilide, the carboxyl group may therefore be tertiary.

4. Taking the tetracyclic structure to be correct the $(R_L)_D$ of the methyl ester becomes 70·01 which differs from the calculated value 69·33 (due allowance being made for the *cyclo*-butane ring). The difference of 0·67 unit may be explained on the ground that the substance is always mixed with the isomeric β-santalic acid which contains two double bonds (part V) and consequently possesses a higher refractive index and a lower density—characteristic of the β-series. An examination of Lorenz's formula $(R_L)_D = \frac{n^2-1}{n^2+2} \times \frac{M}{D}$ will indicate that if under some circumstances n decreases and D increases, as will be the case, if Guerbet's acid is freed from β-santalic acid, there will be a sharp fall in the observed molecular refractivity. The difference between the calculated and observed values may then vanish.

As Guerbet's acid is different from α-santalic acid a new name γ-santalic acid is, therefore, suggested for it.

EXPERIMENTAL

Isolation of Guerbet's Acid.—Government-certified sandalwood oil (7 lbs.) was saponified by boiling for ½ hour with sufficient amount of alcoholic potash (3%). Excess of alcohol was then distilled off and the residual oil poured into water contained in a big separating funnel, shaken thoroughly and then allowed to stand. The aqueous layer was separated and the oily layer was again extracted with water. The combined aqueous liquor was evaporated on the water-bath to a smaller bulk and shaken three times with sufficient amount of ether to remove any oily substance. The alkaline aqueous liquor was then acidified with cold dilute sulphuric acid and the oily acid layer which separated was taken in ether. The ethereal layer

after washing, was dried with anhydrous calcium chloride, filtered and fractionated under reduced pressure in a Claisen's flask to which a 18 cm. bulb-fractionating column had been fused. The distillate was collected in three fractions as follows:

Fraction A: b.p. up to 150°/1mm., mostly teresantalic acid
,, B: b.p. 150°-172°/1mm., mostly Guerbet's acid
,, C: b.p. 172°-188°/1mm., mostly β-santalic acid

Most of the Guerbet's acid was in fraction B. Fraction A on redistillation gave a higher boiling fraction which was added to the fraction B. The combined amount was then refractionated three times in a smaller flask with similar bulb arrangement and the fraction boiling at 166°/1 mm. was collected; yield 12·3 g.; b.p. 166°/1 mm.; 189°/9 mm.; $n_D^{26.5}$, 1·5021; n_D^{30}, 1·5055. The substance is thick syrupy in nature, insoluble in water and has a persisting smell. Silver salt, prepared in the usual way, is fairly stable towards light at the ordinary temperature. The substance is a weak acid and cannot be titrated with alkali. Equivalent weight was determined by ignition of the silver salt. (Found: Equiv., 235·30. C, 76·29; H, 9·72. $C_{15}H_{22}O_3$ requires C, 76·88; H, 9·46 per cent. Equiv. 234·49)).

Methyl ester was prepared from the silver salt and methyl iodide in absolute methyl alcoholic medium; b.p. 141°/9 mm.; n_D^{25}, 1·4892; n_D^{30}, 1·4915: d_4^{20}, 1·02858; d_4^{25}, 1·02483; $(R_L)_D$, 70·01. (Found: C, 77·20; H, 9·91. $C_{16}H_{24}O_2$ requires C, 77·38; H, 9·77 per cent).

Santalal.—Chromic acid (4 g.) in glacial acetic acid (30 c.c.) was added to an ice-cold solution of pure α-santalol (10 g.) in glacial acetic acid (25 c.c.) and the solution stirred thoroughly for 15 minutes and then warmed on the water-bath for about 10 minutes. The oxidised mixture was poured into sufficient amount of water and extracted with ether. The ethereal solution was washed thoroughly with water, dried with calcium chloride, filtered and distilled in vacuum. α-Santalal distilled at 153°/10 mm.; yield 4 g.

The *oxime*, prepared in the usual way, melted at 103°.

Nitrile.—The oxime (10 g.) was slowly refluxed for 2 hours with acetic anhydride (50 c.c.). Excess of the anhydride was decomposed with cold water. The nitrile was extracted with ether and purified by vacuum distillation, b.p. 163°/9 mm.; yield 5-6 g.

α-Santalic acid.—The nitrile was dissolved in 15% alcoholic potash (200 c.c.) and refluxed on the water-bath for 12 hours. α-Santalic acid, formed by the hydrolysis of the nitrile, was isolated in the usual way, b.p. 193°/9 mm.; n_D^{30}, 1·5055.

Methyl ester was prepared from the silver salt and methyl iodide, b.p. 147°/9 mm.; (corrected); n_D^{30}, 1·4910; d_4^{20}, 1·0021.

Absorption Spectra of Guerbet's Acid.—Methyl ester of Guerbet's acid was used in this investigation, purified carbon tetrachloride freed from chloroform being employed as the solvent. The absorption spectra were taken with the help of a Hilger Quartz Spectrograph in conjunction with a Specker photometer. Ilford's hyperpanchromatic plates (HP_2) were used for the photographs. Though the photographic density of the two spectra in juxta-position can be compared fairly accurately, still the probability of error in the value of extinction coefficient is certainly +5 to +10%. The molecular extinction coefficient was calculated from the equation

$$I = I_0 \times 10^{-Em.c.d}$$

where I and I_0 are the intensities of transmitted and incident light; c is the concentration in gram mols./liter; d the thickness of the absorption cell in cm. The results have been plotted graphically.

Further work in this line to prepare some pure Guerbet's acid freed from the unsaturated impurities by ozonisation and the subsequent systematic examination of the pure compounds and its derivatives is in progress.

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STUDIES IN THE SANTALOL SERIES. PART V. ISOLATION OF β-SANTALIC ACID, A NEW CONSTITUENT OF SANDALWOOD OIL

BY S. C. BHATTACHARYYA

A new monobasic acid of the molecular formula $C_{15}H_{22}O_2$ has been isolated from sandalwood oil. The substance contains two double bonds and consequently possesses a bicyclic structure and has been named β-santalic acid. The absorption spectra of the substance in the ultraviolet region have been investigated.

Among the different constituents of East Indian sandalwood oil which have so far been isolated (Simonsen, "Terpenes", Vol. II, p. 544) β-derivatives form a comparatively minor part. Except β-santalol and β-santalene all the other ingredients of the oil, so far isolated, are more or less connected with the tricyclic alcohol, α-santalol and its derivatives. About 4 g. of a new monobasic acidic substance of the molecular formula $C_{15}H_{22}O_2$ have now been isolated from the East Indian sandalwood oil. As revealed by oxidation with percamphoric acid, the substance contains two double bonds and consequently possesses a bicyclic ring structure. In all probability the substance appears to be the corresponding carboxylic acid of β-santatol and has therefore been named β-santalic acid. It is necessary to mention in this connection that the acid is an unknown substance and though β-santalol can be isolated in a pure state it has not been possible up till now, to prepare β-santalic acid from it. The preparation involves about 5 successive synthetic operations necessitating the use of a considerable amount of β-santalol which it is difficult to procure. A comparative study of this substance and its derivatives with those of α-santalic acid has been made. The results are shown in Table I.

TABLE I

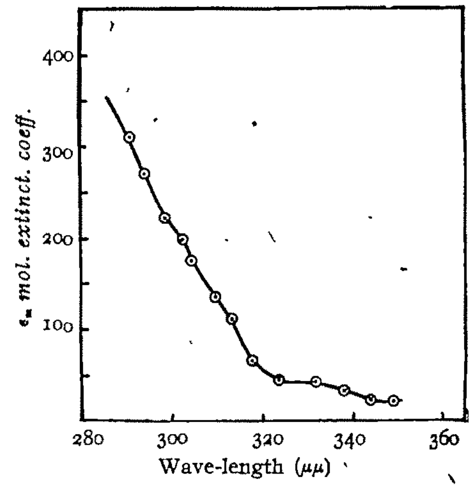
Name	Boiling point.	Difference in boiling point.	n_D^{20}.	Difference in n_D^{20}.
α-Santalol	155°/9 mm.	38°	1·5037	0·0018
α-Santalic acid	193°/9 mm.		1·5055	
Me-α-santalate	147°/9 mm.	46°	1·4910	0·0145
β-Santalol	163°/9 mm.	39°	1·5120	0·0016
New acid	202°/9 mm.		1·5136	
Me-ester of new acid	157°/9 mm.	45°	1·4989	0·0147

Thus, it is seen that the relationship existing between the boiling points and refractive indices of α-santalol, α-santalic acid and its methyl ester is quite analogous to that existing between β-santalol, the new acid and its methyl ester. It is also well known that the β-deri-

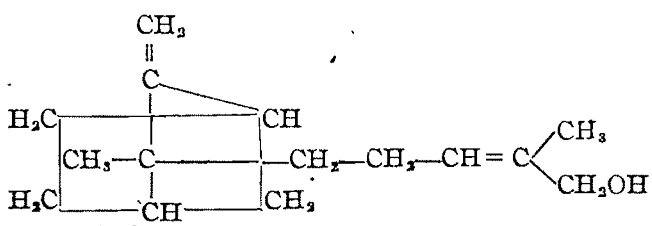
vatives of the santalol series contain two double bonds and consequently higher refractive indices than the corresponding compounds of the α-series, all of which contain only one ethylenic linkage. As shown in Table II, the difference between the values of the refractive indices of the santalols, santalic acids and their methyl esters is almost identical. This proves that there exists an additional double bond in the new acid.

TABLE II

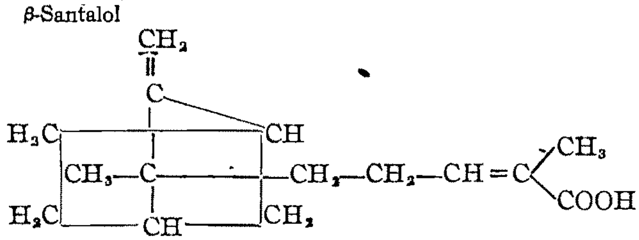
Name	n_D^{30}.	Change in n_D^{30}.
α-Santalol	1·5037	0·0083
β-Santalol	1·5120	
α-Santalic acid	1·5055	0·0080
New acid	1·5135	
Me-α-santalate	1·4909	0·0080
Me-ester of new acid	1·4989	



As stated before, oxidation with percamphoric acid reveals the existence of two double bonds in the new acid. The absorption spectrum of the substance in the ultraviolet region has also been investigated. The substance shows strong absorption as indicated from the stiff nature of the curve. In conformity with the structure of β-santalol (Ruzicka, *Helv. Chim. Acta*, 1935, **18**, 1835), the following structure has been suggested for the new acid.



β-Santalol



β-Santalic acid

EXPERIMENTAL

Isolation.—The acid was isolated from fraction C (*vide* Part IV). The small amount of higher boiling liquid, which was obtained after redistillation of Guerbet's acid, was mixed with the fraction C. The total amount (about 7 g.) was then fractionated thrice from a 10 c.c. Claisen's flask to which a 12 cm. bulb-fractionating column had been fused. The portion coming at 181°/1 mm. was collected. Yield 4 g. from 7 lbs. of oil (Found: C, 76·41; H, 9·6. $C_{15}H_{22}O_2$

requires C, 76·88; H, 9·46 per cent.) B.P. 181°/1 mm.; 202°/9 mm.; $n_D^{28.5}$, 1·5100; n_D^{20}, 1·5136; unsaturation number, 1·90. The substance is thick and syrupy in nature and insoluble in water. It smells exactly like Guerbet's acid. The silver salt is insoluble in water and is fairly stable towards light at ordinary temperature.

This is a weak acid and cannot be correctly titrated with alkali. Equivalent weight was found by ignition of the silver salt. (Found: Equiv., 233·9 $C_{15}H_{22}O_2$ requires Equiv., 234·49).

Methyl ester $C_{15}H_{21}O_2$ (CH_3) was prepared from the silver salt and methyl iodide in the usual way; b.p. 157°/9 mm.; n_D^{25}, 1·4969; n_D^{20}, 1·4989. (Found: C, 77·6; H, 9·77. $C_{16}H_{24}O_2$ requires C, 77·38; H, 9·7 per cent).

Absorption spectrum was determined by following the same procedure as in the case of Guerbet's acid (*cf.* Part IV).

Further work for the complete elucidation of the structure of this compound is in progress.

The author's thanks are due to the Government of Mysore for kindly supplying some sandalwood oil for further investigation of this substance as also that of Guerbet's acid. The author is also indebted to Prof. P. C. Guha for his interest during the investigation.

ORGANIC CHEMISTRY LABORATORIES,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

Received June 2, 1944.

STUDIES IN THE SANTALOL SERIES. PART VI. A NOTE ON THE PARACHOR OF FUSED RING STRUCTURE

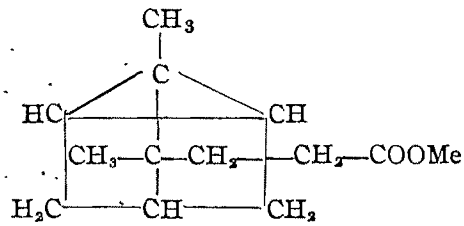
BY P. C. GUHA AND S. C. BHATTACHARYYA

Only a limited amount of work has been done about the parachor of compounds containing fused ring structures with some of the carbon atoms being common to more than one ring. Deshapande and others (*J. Indian Chem. Soc.*, 1942, **19**, 157) by using *iso*nitrosocamphor in nitrobenzene solution have proved the additive nature of parachor in fused-ring compounds.

Substances more complicated than *iso*nitrosocamphor are easily obtainable among the compounds of the santalol series. In connection with our researches in the santalol series, the parachor of a typical compound of this series *viz.* that of the methyl ester of tri*cyclo*-ekasantalic acid has been determined. The substance possesses a fused tricyclic ring structure and is a liquid under ordinary conditions. The pure ester was prepared according to the method of Semmler (*Ber.*, 1907, **40**, 1120, 1124), b.p. 127°/10 mm.; n_D^{20}, 1·4785; d_4^{20}, 1·0166; Molecular formula $C_{13}H_{20}O_2$; Mol. Wt. 208·29. Surface tension of the substance was determined by the drop method, Traube's stalagmometer being used for this purpose, pure bi-distilled water was used as the reference liquid. Density of the ester at different temperatures was determined with a very small pyknometer; parachor was calculated in the usual way.

Temp.	Surface tension of ester.	Mol. Wt.	Density.	Parachor (*P*)	Mean (*P*)
20°	34·99	208·29	1·0166	497·7	497·0
30°	33·47	208·26	1·00737	496·3	

The theoretical value of parachor was calculated in the usual way from the structure of methyl ester of tri*cyclo*ekāsantalic acid (I).



Methyl-tri*cyclo*ekasantalate
$C_{13}H_{22}O_2$
(I)

Calculated parachor ;

13C	4·8×13 =	62·4
20H	17·1×20 =	342·0
O_2 (in ester)	60 =	60·0
1 three-membered ring	=	16·7
2 five-membered rings	8·5×2 =	17·0
Total	=	498·1

Thus the theoretically calculated value is found to agree closely with that obtained from the surface tension of the substance. Therefore, it can be concluded that in the parachor of a compound containing fused ring structure, all the rings play their parts separately as independent units, the carbon atoms common to more than one ring having no additional influence whatsoever.

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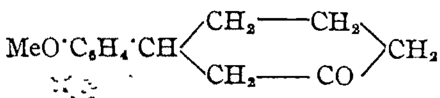
DERIVATIVES OF 3-(p-METHOXYPHENYL)-CYCLOHEXANONE

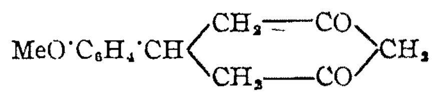
By Piyus Kanti Chaudhuri

A method of preparation of 3-(*p*-methoxyphenyl)-*cyclo*hexanone from 5-*p*-methoxyphenyldihydroresorcinol is recorded. Banerjee's claim to the synthesis of the above ketone could not be confirmed. The ketone, prepared by him, is shown to be 3-(*p*-methoxyphenyl)-Δ^2*cyclo*hexanone, synthesised from ω-chloro-*p*-methoxypropiophenone and ethyl sodioacetoacetate.

In connection with certain investigations which are in progress in these laboratories it seemed desirable to obtain a supply of 3-(*p*-methoxyphenyl)-*cyclo*hexanone (I). The present communication deals with a number of experiments which led to the development of a satisfactory preparative method for this ketone which does not appear to have been made hitherto.



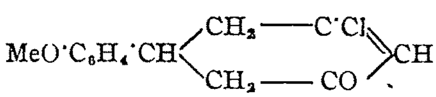
(I)



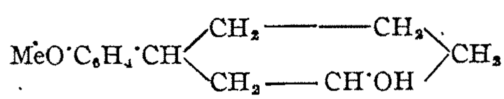
(II)

A perusal of the work of Crossley and his co-workers (*J. Chem. Soc.*, 1907, **91**, 63; 1911, **99**, 1101; also Byod, Clifford, Probert, *ibid.*, 1920, **117**, 1388) on the synthesis of substituted *cyclo*hexanones suggested that 5-*p*-methoxyphenyldihydroresorcinol (II) might prove to be a valuable intermediate for the preparation of the ketone (I), more particularly since, the substituted dihydroresorcinol (II) can now be prepared in any desired quantity (Vorländer, *Annalen*, 1897, **294**, 310; Hinkel, Ayling and Dippy, *J. Chem. Soc.*, 1935, 540) by the condensation of anisalacetone with ethyl sodiomalonate (Vorländer's reaction) followed by hydrolysis of the resulting product and subsequent removal of carbon dioxide (Friedmann, *J. prakt. Chem.*, 1936, *ii*, **146**, 65).

On treatment with phosphorus trichloride in presence of dry chloroform 5-*p*-methoxyphenyldihydroresorcinol (II) behaves in the expected manner (*cf.* Crossley and Le Sueur, *J. Chem. Soc.*, 1903, **83**, 494; 1905, **87**, 1488), and yields 5-chloro-3-(*p*-methoxyphenyl)-Δ^5-*cyclo*hexanone (III), m.p. 70°. The latter on reduction with sodium and moist ether



(III)



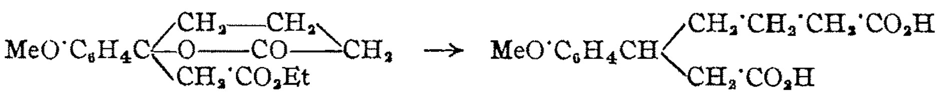
(IV)

gives 3-(*p*-methoxyphenyl)-*cyclo*hexanol (IV), m p. 83-84° in a moderate yield. This on oxidation with Beckmann's chromic acid mixture, in the usual way, affords the desired ketone (I), b.p. 153-54°/4 mm. (*semicarbazone*, m.p. 193-94°).

Owing to the many steps involved the overall yield of the ketone (I) obtained in the above series of reactions is not, however, so good as could be desired. This difficulty is finally overcome by directly hydrogenating the chloroketone (III) in presence of colloidal palladium (Skita and Franck, *Ber.*. 1911, **44**, 2862; France, Heilbron and Hey, *J. Chem. Soc.*, 1940, 1219) which proves to be most suitable for the preparation of the ketone (I) in appreciable quantities.

The properties of the ketone, thus obtained, are, however, quite different from those attributed to 3-(*p*-methoxyphenyl)-*cyclo*hexanone prepared by Banerjee (*J. Indian Chem. Soc.*, 1940, **17**, 576) by another route.

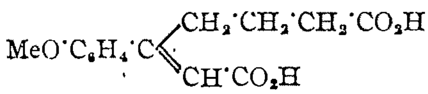
In view of this it seemed desirable to re-examine the work of Banerjee (*loc. cit.*). Banerjee prepared his ketone through the following series of reactions: Ethyl γ-anisoylbutyrate on treatment with ethyl bromoacetate and zinc yielded the unstable δ-lactonic ester (V), which was reduced with zinc dust and caustic soda to give a crystalline acid; m.p. 154-55°, which Banerjee regarded as β-(*p*-methoxyphenyl)-pimelic acid (VI). The latter on ketonisation under the customary experimental conditions (Dieckmann's reaction) furnished 3-(*p*-methoxyphenyl)-*cyclo*hexanone (I).



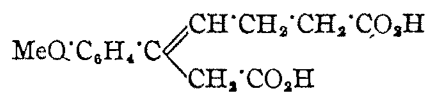
(V) (VI)

It is now found, however, that the δ-lactonic ester (V) on boiling with alcoholic potash *alone* undergoes hydrolysis with the formation of the crystalline acid, m.p. 153-54° described by Banerjee (*loc. cit.*). Clearly, the acid is unsaturated, since it rapidly decolourises bromine and permanganate, a fact apparently overlooked by Banerjee.

Obviously, the unsaturated acid, m.p. 154-55° can have either of the formulae (VII) or (VIII).



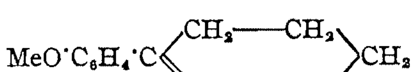
(VII)



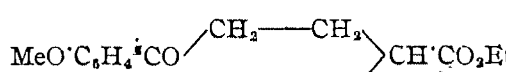
(VIII)

The corresponding diethyl ester, moreover, readily absorbs *one* equivalent of hydrogen in presence of Adam's platinum oxide catalyst at the ordinary temperature with the formation of a saturated ester (as VI) which on hydrolysis, affords β-(*p*-methoxyphenyl)-pimelic acid (VI), m.p. 82-83°. The latter on ketonisation with acetic anhydride (Blanc's reaction) smoothly furnishes 3-(*p*-methoxyphenyl) -*cyclo*hexanone (I), identical in every way with the product described above.

The unsaturated acid (VII) or (VIII), m.p. 154-55°, on the other hand, under similar conditions furnishes a solid ketone, m.p. 84°, (*semicarbazone*, m.p. 218-19°), evidently, identical with Banerjee's ketone (*loc. cit.*). It would appear from the foregoing observations, that the solid ketone, first prepared by Banerjee, must be correctly represented as 3- (*p*-methoxyphenyl)- Δ^2-*cyclo*hexenone (IX). This also follows, because, the latter on hydrogenation over



(IX)



(IX)

Adam's catalyst is quantitatively converted into 3- (*p*-methoxyphenyl) -*cyclo*hexanone (I).

In order to obtain further evidence on this point, the unsaturated ketone (IX) has been synthesised by the action of ω -chloro-*p*-methoxypropiophenone (Kenner and Statham, *J. Chem. Soc.*, 1935, 301) on ethyl sodio-acetoacetate followed by simultaneous hydrolysis and ring-closure of the resulting product by means of dilute sodium hydroxide.

The foregoing synthesis which leaves no room for doubt regarding the structure of the unsaturated ketone is precisely analogous to the formation of 3-phenyl- Δ^2-*cyclo*pentenone from ethyl phenacylacetoacetate (Borsche, *Ber.*, 1908, **41**, 194).

EXPERIMENTAL

5-*p*-Methoxyphenyldihydroresorcinol (II) required was prepared by the condensation of anisalacetone ("Organic Synthesis" Vol. I, p. 71) with ethyl sodiomalonate in the usual way. The condensation product is best hydrolysed according to the method of Friedmann (*loc. cit.*). It has m.p. 184° after one crystallisation from dilute acetic acid. Hinkel, Ayling, and Dippy (*loc. cit.*) give m.p. 175° (decomp.).

5-*Chloro*-3- (*p-methoxyphenyl*)- Δ^5 -cyclo*hexenone* (III).—A mixture of 5-*p*-methoxyphenyldihydroresorcinol (65·4 g.), dry chloroform (160 c.c.) and phosphorus trichloride (15 c c.) was heated under reflux on the water-bath for 4 hours. The excess of chloroform was distilled off on the water-bath, the residue was mixed with ice-water and repeatedly extracted with ether. The ethereal solution was washed successively with a 4% solution of sodium hydroxide and water, dried, and evaporated. The residual brown oil was carefully distilled under reduced pressure when almost the whole quantity boiled at 210°/11 mm. and solidified to a crystalline mass. On recrystallisation from light petroleum (b.p. 60-80°) it formed beautiful, colourless needles, m.p. 70°, yield, 34·4 g. (Found: Cl, 14·9. $C_{13}H_{13}O_2Cl$ requires Cl, 15·01 per cent).

3- (p-*Methoxyphenyl*) -cyclo*hexanol* (IV).—Sodium (9 g.), cut into thin slices, was gradually introduced to a solution of the foregoing chloroketone (6·4 g.) in ether (100 c.c.) kept over water (100 c.c.) contained in a flask provided with a reflux condenser through which ice-cold water was allowed to circulate. When no more unreacted sodium remained the ethereal solution was separated, washed with water, dried over potassium carbonate and distilled. 3- (*p-Methoxyphenyl*) -cyclo*hexanol* distilled at 165°/5 mm. as a colourless liquid which quickly solidified to a crystalline mass. On purification from light petroleum (b.p. 60-80°) it formed transparent needles, m.p. 83-84°. (Found: C, 75·21; H, 8·73. $C_{13}H_{18}O_2$ requires C, 75·71; H, 8·74 per cent).

3-(p-*Methoxyphenyl*) -cyclo*hexanone* (I). (1) *From* 3-(p-*Methoxyphenyl*) -cyclo*hexanol* (IV).—The alcohol (14 g.) was well shaken with an excess of Beckmann's chromic acid mixture (126 g.), the mixture became warm and in a few minutes the oxidation was complete. The whole was finally warmed to 50°-60° for ½ hour, cooled, diluted with water and repeatedly extracted with ether. The ethereal solution was washed with water, dried and evaporated. The residual oil was purified by distillation under reduced pressure. 3- (*p*-Methoxyphenyl)-*cyclo*hexanone formed a colourless, refracting liquid, b.p. 155°/4 mm.

(2) From 5-*Chloro*-3- (p-*methoxyphenyl*)-Δ^5-cyclo*hexanone* (III).—The chloroketone (34·4 g.) dissolved in absolute alcohol (150 c.c.) was shaken in an atmosphere of hydrogen with the addition of gum arabic (0·3 g.), dissolved in a little water, and palladium chloride (0·3 g.) until one equivalent of hydrogen was taken up. The catalyst was filtered off, and the excess of solvent evaporated. The residual oil on distillation under reduced pressure gave 3- (*p*-methoxyphenyl) -*cyclo*-hexanone (25 g.) as a colourless liquid, b.p. 153-54°/4 mm. (Found: C, 76·0; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·47; H, 7·86 per cent). The *semicarbazone* crystallises from rectified spirit in clusters of glistening prisms, m.p. 193-94°. (Found: C, 63·8; H, 7.2. $C_{14}H_{19}O_2N_3$ requires C, 64·2; H, 7·2 per cent).

Condensation of Ethyl γ-Anisoylbutyrate with Ethyl Bromoacetate : Formation of the Unsaturated Acid (VII or VIII).—Ethyl γ-anisoylbutyrate (14 g.), ethyl bromoacetate (10 c.c.), zinc wool (7·5 g.), and benzene (45 c.c.) were heated under reflux with the addition of a crystal of iodine as described by Banerjee (*loc. cit.*). The product was decomposed

with ice and an excess of dilute sulphuric acid, the benzene layer was isolated, washed with water, and then repeatedly extracted with a 10 % solution of caustic soda until a test portion no longer gave any turbidity on acidification. The alkaline solution was acidified and extracted with ether. The ethereal solution was washed, dried and distilled. The residual viscous oil (12 g.) was hydrolysed by boiling with an excess of 10 % alcoholic potash (3 mols.). The excess of alcohol was removed from the water-bath as completely as possible. The alkaline solution was extracted with ether in order to remove neutral impurities, seperated, and cautiously acidified with hydrochloric acid. The solution was then extracted several times with ether, the ethereal solution washed, dried, and evaporated. The residue (10 g.) solidified on scratching. The benzene solution on evaporation yielded a small residue (5g.) which eventually solidified and proved to be the unchanged keto-ester. The crude acid (10 g.) obtained was esterfied with alcohol (75 c.c.) and concentrated sulphuric acid (5 c.c.) in the usual way. The ethyl ester formed a colourless liquid, b. p. 189-92°/4mm., yield 6·7 g. It rapidly decolourises a solution of bromine in carbon disulphide.

Hydrolysis with Alcoholic Potash.—The ester (1 g.) was refluxed with an excess of 10 per cent alcoholic potash (3 mols.),the excess of alcohol was removed on the water-bath. The alkaline solution was extracted with ether, acidified with dilute hydrochloric acid and repeatedly extracted with ether. The ethereal solution was washed with water, dried and evaporated. The residue on keeping in an evacuated desiccator solidified to a crystalline mass and on purification from aqueous alcohol (charcoal) formed colourless crystals, m p. 154-55°. A solution of the unsaturated acid in sodium carbonate rapidly decolourises potassium permanganate solution. (Found: C, 63·5; H, 6·3. $C_{14}H_{16}O_5$ requires C, 63·63; H, 6·1 per cent).

β-(p-Methoxyphenyl)-pimelic Acid. (VI)—The foregoing unsaturated ester (4·7 g.) dissolved in absolute alcohol (20 c.c.) was shaken in an atmosphere of hydrogen with Adam's platinum oxide catalyst (0·05 g.) until the calculated quantity of hydrogen (375 c.c.) was absorbed. The solution was filtered from the platinum which was also washed once with alcohol. The excess of alcohol was removed and the residual oil on distillation yielded *ethyl β-(p-methoxyphenyl)-pimelate* (4·5 g.) boiling at 199°/5mm. (Found: C, 66·6; H, 8·1. $C_{18}H_{26}O_5$ requires C, 67·1; H, 8·1 per cent). The *ester* on hydrolysis with an excess of 10 % alcoholic potash in the usual way gave the acid as a crystalline solid which on recrystallisation from a mixture of benzene and petroleum ether (b.p. 80°-100°) formed minute prisms, m.p. 92-93°. (Found: C, 63·3; H, 6·9. $C_{14}H_{18}O_5$ requires C, 63·16; H, 6·7 per cent).

Ketonisation.—The acid (5 g.) was heated with an excess of acetic anhydride under reflux on the sand-bath for 5 hours. The excess of acetic acid and acetic anhydride was then removed at the water pump and the residue distilled in an oil-pump. The ketone had b.p. 156-58°/5mm. yield 65 per cent. It was characterised as 3-(p-methoxypheny)-*cyclo*hexanone by its b.p. and by the preparation of the semicarbazone, m.p. 193-94°.

The *unsaturated acid*, m.p. 154-55°, on ketonisation yielded a crystalline *unsaturated ketone*, m.p. 84°, (*semicarbazone*, m.p. 218-19°) evidently identical with Banerjee's ketone (*loc. cit.*).

Condensation of ω-Chloro-p-methoxypropiophenone with Ethyl Sodio-acetoacetate: Formation of 3-(p-*Methoryphenyl*)-Δ^2cyclo*hexenone* (IX) —Molecular sodium (1·72 g.) covered with benzene (20 c.c.) was cooled in ice and gradually mixed with ethyl acetoacetate (2·7 g.) and the product left overnight. A solution of ω-chloro-*p*-methoxypropiophenone (Kenner and Statham, *loc. cit.*) (14·8 g.) was then added and the reaction allowed to proceed at the room temperature overnight. It was then heated on the steam-bath for 5-6 hours to complete the

reaction. On cooling the product was treated with ice and dilute hydrochloric acid. The benzene layer was removed, washed, dried, and the solvent evaporated. The residue (21 g.) consisting of a brown viscous oil could not be distilled without decomposition. The crude product (5 g.) was mixed with a solution of sodium hydroxide (2 g.) in water (200 c.c.) and the whole heated to boiling under reflux for 1 hour. It was cooled and extracted with ether. The ethereal solution was washed, dried, and distilled. The residue on distillation under reduced pressure yielded a pale yellow oil (2 g.), b.p. 173°/4mm. which rapidly solidified. On recrystallisation from petroleum ether (b.p. 60°-80°) with the addition of a few drops of ethyl acetate it had m.p. 84° and consisted of 5-(*p-methoxyphenyl*)-Δ^2-cyclo*hexenone*. (Found: C, 76·8; H, 6·79. $C_{13}H_{14}O_2$ requires C, 77·0; H, 6·9 per cent). There remained in the distillation flask a solid residue which was not further examined.

The *semicarbazone*, prepared in the usual way, crystallises from dilute alcohol, m.p. 218-19°. (Found: C, 64·2; H, 7·2. $C_{14}H_{17}O_2N_3$ requires C, 65·0; H, 6·6 per cent).

The above unsaturated ketone on hydrogenation with Adam's platinum oxide catalyst rapidly absorbs one molecule of hydrogen giving 3-(*p*-methoxyphenyl)-*cyclo*hexanone (I), which was identified by the formation of the semicarbazone, m.p. and mixed m.p., 193-94°.

Further work is in progress.

My best thanks are due to Dr. J. C. Bardhan for his kind interest in the progress of the work.

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ESTIMATION OF BISMUTH. PART VI. COLORIMETRIC ANALYSIS WITH PHENYDITHIOBIAZOLONE THIOL

BY ANIL KUMAR MAJUMDAR

Bismuth has been estimated both colorimetrically and gravimetrically with the reagent phenyldithiobiazolone thiol. Maximum absorption of the colour system has been found to be at 460 mμ. The colour system has been found to obey Beer's law through a long range of concentration of bismuth. Effect of diverse ions has also been studied.

Like dimercaptothiobiazole, the reagent phenyldithiobiazolone thiol ($C_8H_6N_2S_3$) having the reacting group RN-CS-S-C-(SH)-N, has been found to give coloured precipitates with the metals of the sulphide group. It gives yellow precipitates with gold, mercury, lead, silver, platinum, arsenic and antimony, white with cadmium and zinc, brown with copper, brick red with tin and red with bismuth and palladium.

Dubsky and Trtilek (*Z. anal. Chem.*, 1934, **96**, 412) used this reagent for the detection of small quantities of bismuth, their identification limit being 1·2 μg. and sensitivity 1 part in 28,000 parts. Air dried bismuth salt of the reagent were found by them to be of composition $Bi(C_8H_5N_2S_3)_3$, $2H_2O$, which when heated in air at 100° loses 3·09% of water.

The author (*J. Indian Chem. Soc.*, 1942, **19**, 396) however, has observed that the coloration limit can be extended to 1 part in 6000,000 parts if nitric acid solution is used and not chloride solution as used by Dubsky and others (*loc. cit.*) and that bismuth to the extent of 3 γ in 20 c.c. solution can be accurately estimated colorimetrically with this reagent as the colour system obeys Beer's law through a long range of concentration studied. Further, phenyldithiobiazolone thiol is found to be a suitable reagent for the gravimetric estimation of bismuth as the bismuth compound of the reagent is stable and of definite composition. The air dried compound on heating to 105° has been found to lose only 2·94% of water even on heating for several hours. No further loss in weight was observed on heating this up to 130°. This suggests that the bismuth compound, which was heated at 105°, is of composition $Bi(C_8H_5N_2S_3)_3$, $\frac{1}{2}H_2O$,

With the help of a Dubosq colorimeter, bismuth has been estimated colorimetrically and also the effect of diverse ions on the colour system has been studied.

With a spectrophotometer the peak of the absorption band of the colour system has been found to be at 460 mμ and that it obeys Beer's law has further been verified by the fact that a straight line resulted when the logarithms of the transmittances at 460 mμ has been plotted against the respective concentrations.

Effect of organic solvents on the compounds, formed by the reagent with the metals of the sulphide group, has also been examined with the idea of separating bismuth from other elements.

Reagents.—Reagents that were used during these experiments were the same as used during the colorimetric analysis of bismuth with dimer captothiobiazole (Part IV of this series).

Phenyldithiobiazolone thiol ($C_8H_6N_2S_3$) was prepared as potassium salt (m.p. 250°) and recrystallised (Busch, *Ber.*, 1894, 27, 2511). This was kept in an orange coloured desiccator. A 0·5 per cent solution of potassium salt of the reagent in water was prepared. This solution was colourless but on keeping for several days, a slight opalescence was observed.

EXPERIMENTAL

With dimercaptothiobiazole (*loc. cit.*), nitric acid, up to a certain limit (5 c.c. normal nitric acid in a volume of 20 c.c.), has been found to intensify the colour. But here no influence of nitric acid on the colour system has been observed, even when one c.c. of concentrated nitric acid (65%) in a volume of 20 c.c. was present. Like dimercaptothiobiazole, an excess of the reagent solution of gum acacia has no influence on the colour system.

During the colorimetric estimation of bismuth by the reagent phenyldithiobiazolone thiol it has been observed that if the amount of bismuth is less than $3{\cdot}5\times10^{-4}$g. solution of gum acacia need not be used. But for bismuth of higher amount, gum acacia solution should be used to stabilise the colloidal suspension of the compound formed with the reagent. With this reagent full development of maximum colour intensity takes place in a minute or two.

General Procedure

In the tube of a Dubosq colorimeter were taken a few c.c. of the bismuth nitrate solution containing some free nitric acid to keep the bismuth in solution, one c.c. of gum acacia solution, a few c.c. of water and then a few drops of the reagent solution (about 1 c.c.), drop by drop, with shaking, till no further development of colour was noticed. The volume of the solution was maintained at 20 c.c. After thorough mixing the colour was compared. If the bismuth solution contains ions other than nitrate, 5 c.c. of normal nitric acid should be added to the solution along with 5 c.c. of gum acacia solution. Results are given below.

Bi taken.	Bi found.	Error.	Bi taken.	Bi found.	Error.
6·48 mg.	6·46 mg.	−0·02 mg.	0·259 mg	0·256 mg.	−0·003
3·888	3·920	+0·032	0·1037	0·1037	Nil
2·592	2·580	−0·012	0·065	0·066	+0·001
1·296	1·30	+0·004	0·0065	0·0065	Nil
0·518	0·524	+0·006	0·0039	0·0040	+0·0001

For the estimation of one milligram of bismuth or more, one should take the nitric acid solution of bismuth in a 100 c.c. volumetric flask, add a few c.c. of gum acacia solution sufficient to stabilise the colloidal suspension, dilute with water almost

to the mark, add a few c.c. of the reagent solution till there is no further increase in colour and then make up to the mark with water and mix thoroughly. 20 C.c. of this solution are then taken in the colorimeter tube and the colour compared. The same quantities of nitric acid, reagent and gum acacia are added to both the unknown and the standard.

Conformity to Bee'rs law.—That the colour system obeys Beer's law through a long range of concentration is evident from the graphs (Figs. 1 and 2) drawn by plotting the reciprocal colorimetric readings on the abscissa and the concentrations on the ordinates.

Stability of the colour.—As with dimercaptothiobiazole (*loc. cit.*) here also glycerine or agar agar can be used as stabilisers in addition to gum acacia. Gelatine cannot be used as such, as it gives a similar cream coloured precipitate.

The stability of the colour system depends upon the amount of nitric acid and on the amount of bismuth present in exactly the same way as has been observed with dimercaptothiobiazole. But here if the amount of bismuth is less than 3.5×10^{-4} g. it can be estimated without the addition of gum acacia.

Interference.—The effect of diverse ions on the colour system has been studied, in the same way as has been done with dimercaptothiobiazole, with the standard solutions of the ions prepared from the chloride, nitrate or sulphate salts of the cations and from sodium or potassium salts of the anions. Interference of the ions has been determined under the conditions recommended under the general procedure, using bismuth concentration of 0·26 milligram and adding 5 c.c. of normal nitric acid along with 5 c.c. of gum accia to the solution. The effect of nitrate ions was studied by adding only 5 c.c. of gum acacia to the bismuth nitrate solution containing very small quantity of free nitric acid (dilute).

The limiting concentrations of the coloured ions, that interfere only if present at concentrations exceeding that required to produce the colour due to the ion itself, are : Cu^{++}, 0·07mg. ; Co^{++}, 2 mg. ; Ni^{++}, 9 mg.

The following ions are without effect even at a concentration of : Mn^{++}, 100 mg. ; Fe^{++}, 100 mg. ; NO'_3, 100 mg. ; 1 c.c. HNO_3 (sp. gr. 1·4) ; SO''_4, 100 mg. ; C_2O_4'', 100 mg. ; $C_4H_4O_6''$, 100 mg. ; 10 c.c. H_2SO_3 (saturated solution) ; 1 c.c. H_3PO_2 (*d*, 1·274).

The limiting concentrations for the interfering ions due to precipitations are : Zn^{++}, 10 mg. ; Cd^{++}, 0·5 mg. ; Pb^{++}, 1 mg. ; Hg^{++}, 0·5 mg. ; Ag^{++}, 0·3 mg. ; Cl', 50 mg. ; As^{+++}, 0·05 mg. ; Sb^{+++}, 0·1 mg. ; Sn^{++}, 0·2 mg. The concentrations of the interfering ions can be further increased if the concentrations of nitric acid is increased. Thus in presence of phosphate or other ions that form insoluble salts with bismuth, it can be estimated if the precipitate formed is first dissolved in nitric acid. As for example, with 100 mg. of phosphate ions, it has been estimated in presence of 1 c.c. concentrated nitric acid (*d* 1·4) in a volume of 20 c.c.

Estimation of Bismuth in presence of other Ions.—For the estimation of small quantities of bismuth in presence of other interfering ions, it was precipitated as phenyl arsonate (Part IV of this series). From this precipitate bismuth was estimated

in the same way as has been done with dimercaptothiobiazole (Part V of this series) and the results obtained thereby are given below.

Bi taken.	Bi found.	Error.
0·098 mg.	0·097 mg.	−0·001 mg.
0·049	0·049	Nil.
0·0295	0·0292	−0 0003

Solubility of the Salts formed by the metals with the Reagent in Organic solvents.—The bismuth compound is soluble in alcohols such as ethyl, methyl, normal and *iso*propyl and *iso*amyl; and also in ether, chloroform, acetone, pyridine and in ethyl acetate; sparingly soluble in carbon disulphide and insoluble in carbon tetrachloride and in benzene. Compounds formed with copper, cadmium, lead, mercury (ic), antimony and silver are insoluble in ether, *iso*amyl alcohol and in chloroform; compound of cobalt is insoluble in ether and in chloroform but soluble in *iso*amyl alcohol, that of tin (ous) is insoluble in ether, but soluble in *iso*amyl alcohol and in chloroform and that of zinc is soluble in ether, but insoluble in chloroform and in *iso*amyl alcohol.

FIG. 1.

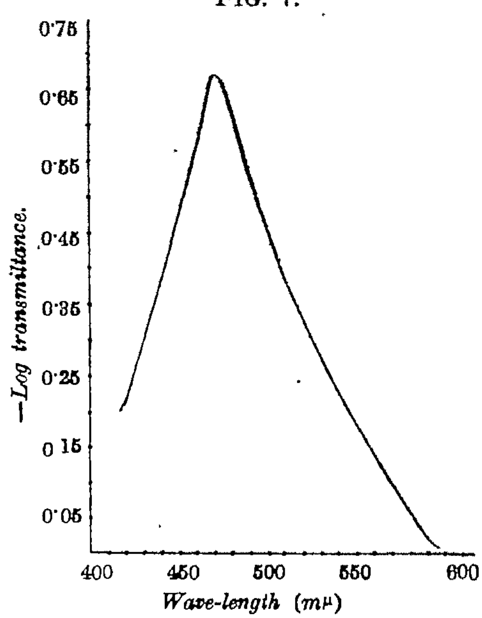
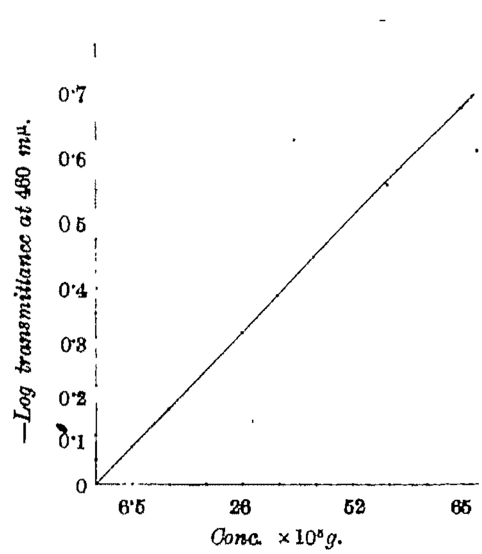


FIG. 2.



Spectrophotometric Study.—Spectrophotometric studies were undertaken with the same instruments and in the same way as with dimercaptothiobiazole (*loc. cit.*). The solution that was used for this contained in a volume of 20 c.c, 0·35 mg. of bismuth nitrate, a little quantity of free nitric acid to keep the bismuth in solution and 2 c.c. of the reagent. When the logarithms of the observed transmittances were plotted against the wave-lengths, peak of the absorption band was found to be at 460mμ (Fig. 1). The reagent solution or the solution of gum acacia had no absorption in the visible region.

Beer's law.—That the colour system also obeys Beer's law has further been verified by plotting the logarithms of the observed transmittances at 460mμ, for a

number of solutions containing from 65 p.p.m. of bismuth, against the respective concentrations (Fig. 2).

As bismuth has been found to be quantitatively precipitated with this reagent from a dilute nitric acid solution containing about 10 c.c. of normal nitric acid per 100 c.c. and the compound formed is stable and of constant composition, a few determinations of bismutn gravimetrically has been undertaken in the following way and thereby good results have been obtained.

To a nitrate solution of bismuth containing 10 c.c. of free nitric acid, (normal) per 100 c c., is added with stirring a few c.c. of one per cent solution of the potassium salt of the reagent in water till no further precipitation takes place. The solution is then heated for some time with stirring till the precipitates coagulate and the solution becomes clear. This is then quickly filtered hot through a porcelain gooch crucible, washed with hot water, dried at 100° and weighed. The weight of the bismuth compound is then multiplied by the factor 0·2340 as the percentage of bismuth in the compound $(C_8H_5N_2S_3)_3$ Bi, $\frac{1}{2}H_2O$ is only 23·4.

Bi taken	Bi found	Bi taken	Bi found
0·0362 g	0·0363 g.	0·0181	0·0180
0·0543	0·0545		

Other elements such as zinc, cadmium, palladium, mercury (ic), lead etc., are quantitatively precipitated by the reagent and further with traces of palladium a red coloration is obtained.

Further works, on the estimation and separation of bismuth from other elements gravimetrically and colorimetrically by extracting with organic solvents as also the estimations of other elements by this reagent are in progress.

My best thanks are due to Prof. P. Rây and to Prof. J. N. Mukherjee for the facilities received in working out this piece of work in their laboratories.

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QUINOLINE DERIVATIVES. PART VII

By T. N. Ghosh, S. L. Lasker and S. Banerjee

For pharmacological study against amoebiasis. 5-iodo-7-chloro-8-hydroxyquinoline. isomeric with Vioform, has been synthesised.

Recently 5-chloro-7-iodo-8-hydroxyquinoline ("Vioform") has been much used in the treatment of certain intestinal infections. The activity of the compound is believed to be due to the liberation of iodine in the intestine. But in case of prolonged administration there is a possibility of iodism and certain other physiological disorders. This liberation of iodine would undoubtedly depend on the stability of the iodo compound and this might vary with the position of the substituent in the benzene ring of the quinoline molecule. In "Vioform" iodine is attached to the 7 position and chlorine at the 5, the latter position being more reactive and stable. It has been considered to be of interest to study the characteristics of a quinoline compound which contains iodine at the 5 position and chlorine at the 7. It may be expected that such a compound would liberate iodine more slowly and as such may exert a more sustained therapeutic activity. With this idea in view 5-iodo-7-chloro-8-hydroxyquinoline has been prepared.

The action of iodine monochloride or chlorine on 8-hydroxyquinoline gives rise to 5 : 7-di-iodo-8-hydroxyquinoline (Papesch and Burtner, *J. Amer. Chem. Soc.*, 1936, **58**, 1314) or the corresponding 5 : 7-dichloro compound (*cf.* Lasker and Ghosh, *Science and Culture*, 1944, **10**, 57). The constitution of the latter compound has been confirmed by its synthesis directly from 2-nitro-4 : 6-dichlorophenol by Skraup's reaction (*cf.* Brunner and Chuard, *Ber.*, 1885, **18**, 445; 1896, **29**, 708). It is, therefore, evident that halogenation of 8-hydroxyquinoline, under ordinary conditions, gives rise to 5 : 7-disubstituted derivative.

The action of iodine monochloride on the potassium salt of 8-hydroxyquinoline at 0° yields a mixture of 5-iodo-8-hydroxyquinoline and the corresponding 5 : 7-di-iodo derivative. This mono-iodo derivative, on chlorination, yields 5-iodo-7-chloro-8-hydroxyquinoline, isomeric with "Vioform."

A certain comparative chemical test (*vide* experimental) indicates that the iodine atom in 5-iodo-7-chloro-8-hydroxyquinoline is more strongly bound than that in "Vioform."

Experimental

5 : 7-*Dichloro-8-hydroxyquinoline*.—(*a*) 8-Hydroxyquinoline (10 g.) was dissolved in alcohol (100 c.c.) and cooled in ice. Dry chlorine gas was passed into the solution till saturated, the colour of the solution changing to yellow. Alcohol was then distilled off on the water-bath and the residual solid was then thoroughly triturated with water and filtered. It crystallised from glacial acetic acid in colour-

less, slender needles, m.p. 178°-179°. (Found : N, 6·32. Calc for $C_9H_5ONCl_2$: N, 6·57 per cent).

(b) 2-Nitro-4 : 6 dichlorophenol (Ling, *J. Chem. Soc.*, 1887, **51**, 787 ; 25 g.) was mixed with dry glycerine (70 g.) and concentrated sulphuric acid (*d* 1·84, 30 g.) and the paste was heated carefully under reflux on a sand-bath under occasional shaking. When the reaction commenced, the sand-bath and burner were removed to avoid too vigorous a reaction. The reaction mixture was allowed to cool and concentrated sulphuric acid (30 g.) was further added. This mixture was heated carefully under reflux on the sand-bath for 4 hours and allowed to cool.

The dark mass was extracted with warm water and after filtration, the clear aqueous solution was treated with excess of sodium carbonate, when a solid (8 g.) was obtained which crystallised from glacial acetic acid (charcoal) in colourless, slender needles, m.p. 178°-179°. Its identity with the previous compound was established by mixed m.p. and analysis.

5-*Iodo*-8-*hydroxyquinoline*.—8-Hydroxyquinoline (14·5 g.) was dissolved in aqueous solution of caustic potash (5·6 g.). The aqueous solution was cooled to 0° and to this an alcoholic solution of iodine monochloride (16·2 g.), cooled to 0°, was gradually added under shaking. A light yellow solid was precipitated which was filtered and washed successively with aqueous solutions of sodium bisulphite, water, sodium thiosulphate and finally water.

The solid was next extracted with boiling alcohol and the insoluble portion, on crystallisation from glacial acetic acid, was proved to be 5 : 7-diodo-8-hydroxyquinoline (m.p. 200°-201°) by a mixed m.p. with a genuine sample, prepared according to the method of Papesch and Burtner (*loc. cit.*)

The clear alcoholic solution was diluted with large quantity of water, when a solid was precipitated which was extracted with ether. The ether solution on distillation, yielded a solid which was purified by solution in ether and distillation of the ether solution. The solid, thus obtained, was crystallised twice from boiling alcohol (charcoal) as a light yellow granular powder (2.5 g.), m.p. 123-24°. (Found : I, 47·01. C_9H_6ONI requires I, 46·86 per cent).

5-*Iodo*-7-*chloro*-8-*hydroxyquinoline*.—5-Iodo-8-hydroxyquinoline (8 g.) was dissolved in dry chloroform (150 c.c.) and cooled to 2°. Dry chlorine gas was then passed into this cooled solution till saturated. A solid was precipitated, which proved to be the hydrochloride of 5-iodo-8-hydroxyquinoline. It dissolved in cold water and the base was precipitated on treatment with sodium carbonate.

The above chloroform solution, after filtration, yielded on distillation a solid which was washed with alcohol and was crystallised twice from glacial acetic acid (charcoal) in cream-coloured (with a yellowish tinge) slender needles, m.p. 147°-148° (deep red colouration), yield 3 g. (Found : Cl, 11·12 ; I, 40·89. C_9H_5 ONCl I requires Cl, 11·63 ; I, 41·63 per cent). Iodine was estimated according to the method of Pearl (*J. Biol. Chem.*, 1943, **148**, 85) and chlorine was estimated by subtracting the corresponding iodine content from the total halogen content determined as silver halide.

When heated slightly with concentrated sulphuric acid, the above compound evolves copious vapour of iodine. Its alcoholic solution gives a deep green colouration with ferric chloride. It gives a green colouration with Million's reagent. When its solution in chloroform is shaken with 10 per cent nitric acid and the mixture allowed to stand for sometime, the chloroform acquires a violet-red colour and the nitric acid becomes somewhat yellow. Similar test with Vioform, under identical conditions, was done and it was found that the chloroform layer acquires the violet-red colour earlier than with the present compound, indicating that possibly the iodine atom in the present compound is more strongly bound than that in Vioform.

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QUINOLINE DERIVATIVES. PART VIII.

By T. N. Ghosh, S. Banerjee and S. L. Lasker

By applying Skraup's reaction some hydroxyquinoline derivatives have been prepared directly from the corresponding nitro compounds.

In connection with some synthetic work, it was found necessary to prepare some chlorohydroxyquinoline derivatives. By following Skraup's method these quinoline derivatives have now been prepared directly from the corresponding nitro compounds. The application of Skraup's reaction in which the amine can be dispensed with and the corresponding nitro compound alone used with success is of interest both from the technical and theoretical point of view, the cost of reduction of the nitro compound being an important factor. Dey and Goswami (*J. Chem. Soc.*, 1919, **115**, 533) have converted nitrocoumarin into related quinolines without using amino coumarin.

The results obtained are summarised below :

Nitro compound (50 g.)	Quinoline derivative	Yield (uncrystallised)	M.p. (Crystallised)	Analysis Found.	Calc.
(1) *o*-Nitrophenol	8-Hydroxyquinoline	5 g.	73-74°	N, 9·48	9·65%
(2) *p*-Nitrophenol	Nil	...	...	...	...
(3) 4-Chloro-2-nitro-phenol	5-Chloro-8-hydroxy-quinoline	18 g.	122°-123°	N, 7·61	7·82%
(4) 4 : 6-Dichloro-2-nitrophenol	5 : 7-Dichloro-8-hydroxyquinoline	16-18 g.	178°-179°	N, 6·84	6·57%
(5) 2-Chloro-4-nitro-phenol	5-Chloro-6-hydroxy-quinoline	14 g.	197°-198°	N, 7·69	7·82%

According to Simon (*Compt. rend.*, 1907, **144**, 138), the mechanism of Skraup's reaction is based on the acrolein produced reacting with amine to give a dihydroquinoline whence by loss of hydrogen quinoline results.

The above scheme of Skraup's reaction is supported by quinaldine synthesis of Doebner and Miller (*Ber.*, 1881, **14**, 2816 ; 1883, **16**, 1664 ; 1884, **17**, 1712). However, this scheme does not explain the synthesis of quinoline derivatives directly from the corresponding nitro compounds.

By heating nitrobenzene with concentrated sulphuric acid, Brunner and Vuilleumier (*Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 434) have obtained *p*-aminophenol-sulphonic acid. This has been explained as being due to an oxygen atom of the nitrobenzene wandering to the *para*-position and then reduction occurring by the sulphur dioxide produced from the sulphuric acid and phenol.

Concentrated sulphuric acid is known to convert alizarin and other hydroxy-derivatives of anthraquinone into tri-and hexahydroxy derivatives. It acts as an oxidising agent. Similarly sulphuric acid can be assumed to be reduced to sulphurous acid, which reduces the nitro compound to the amino compound to start the reaction. Subsequent reduction of the nitro compound to amino derivative after the reaction has once started is possibly due to the hydrogen arising in the reaction as outlined by Simon. The reaction, however, appears to be facilitated by the presence of chlorine atom in the benzene nucleus.

E X P E R I M E N T A L

The quinoline derivatives, described in this paper, are known. The reactions as recorded in this paper have all been carried out under identical experimental conditions. The general method of procedure followed is given below in case of one particular preparation.

5-*Chloro*-8-*hydroxyquinoline*.—Glycerine (140 g.), made anhydrous by heating at 180° (thermometer in liquid) for 30 minutes, was mixed to a paste by shaking with well-powdered 2-nitro-4-chlorophenol (50 g.), to which pure, concentrated sulphuric acid (*d* 1·84 ; 60 g.) was added dropwise with shaking. The mixture was then heated under reflux on a sand-bath with occasional shaking, when a heavy dark liquid was obtained. As soon as the reaction commenced with frothing and evolution of fumes, the flask was taken away from the sand-bath to avoid too vigorous a reaction. After the reaction had subsided, the flask was heated under reflux on the sand-bath for 2 hours with frequent shaking.

The reaction mixture was cooled to room temperature and the lumps were broken. Pure, concentrated sulphuric acid (*d* 1. 84 ; 60 g.) was then added drop by drop with shaking and the mixture was heated under reflux on the sand-bath for 4 hours, the flask being removed from the sand-bath when the reaction tended to become vigorous.

Next day the dark mass was taken out of the flask and thoroughly triturated with sufficient quantity of warm water in a mortar. The mixture was filtered and the clear aqueous solution was treated with sodium carbonate till distinctly alkaline.

A solid was obtained, which was filtered and washed thoroughly with cold water. This operation was repeated two or three times. Total yield 18 g. The product dissolves readily in dilute hydrochloric acid and is precipitated by sodium carbonate. It was crystallised from alcohol (charcoal) in needles, m.p. 122-23°. (Found : N, 7·61. Calc. for C_9H_6ONCl : N, 7·82 per cent).

8-*Hydroxyquinoline.*—In preparing this compound, the reaction mixture was treated with sodium carbonate till distinctly alkaline. The whole mixture was then distilled in steam when the above quinoline derivative was obtained in the distillate. It was filtered and finally crystallised from dilute alcohol in needles, m.p. 73°-74°.

2-*Chloro*-4-*nitrophenol.*—To an acetic acid solution of *p*-nitrophenol (14 g.), cooled in ice, dry chlorine gas was passed till the increase in weight came up to 4 g. The solution was then poured into large quantity of water when a heavy oil was precipitated, which soon solidified on scratching. It was filtered and crystallised from 50% alcohol in colourless rectangular plates, m.p. 110-11°. (Found : N, 7·73. $C_6H_4O_3NCl$ requires N, 8·09 per cent).

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CHARGE AND STABILITY OF COLLOIDS. PART IX. STUDIES ON THE RELEASE OF COUNTER IONS FROM $Fe(OH)_3$ SOL ON THE ADDITION OF PAIRS OF ELECTROLYTES

BY B. P. YADAVA AND A. C. CHATTERJI

The effect of the addition of pairs of electrolytes on release of counter ions from Fe $(OH)_3$ sol has been studied It has been found that in almost all cases the amount of released chlorine is greater than the calculated value. This means that the mixture induces more instability a necessary consequence of which is that there should be no ionic antagonism.

Recently various attempts have been made by several authors (Weiser, *J. Phys. Chem.*, 1931, **35**, 1, 1368 ; Rabinowitsch, *Z. physikal. Chem.*, 1925, **116**, 97 ; and Pauli and others) to follow the changes in the stability of a colloid on the stepwise addition of an electrolyte by determining the amount of counter ions released potentiometrically. In this paper attempts have been made to study the effects of pairs of electrolytes by the above method.

In earlier papers of this series (*J. Indian Chem. Soc.*, 1943, **20**, 115, 219, 223) the release of the counter ions has been studied in some details, when electrolytes having ions of varying valencies are added in single to the hydrous sols of different purity. In this paper the release of counter ions from ferric hydroxide sol has been studied with a view to finding out if any insight into the mechanism of coagulation by electrolyte pairs can be obtained. Electrolyte pairs like $KIO_3+K_2SO_4$; KIO_3+K-citrate ; K_2SO_4+K-citrate have been used. Along with this the release of chlorine ions, when KIO_3, K_2SO_4 and K-citrate are added in singles, is also recorded.

EXPERIMENTAL

Ferric hydroxide sol was prepared by the method given in earlier section of this series (*J. Indian Chem. Soc.*, 1943, **20**, 25, 115). The potentiometric titrations were performed exactly as described before. The volume of the sol taken in each case was 5 c.c., and the total volume of sol and electrolyte mixture was made up to 10 c.c. by adding the requisite volume of distilled water. The maximum amount of the electrolyte added to the fixed volume of the sol was just sufficient to coagulate the sol in an hour. The results obtained are given in the following tables. In these tables the electrolytes have been added up to the coagulation concentration *i.e.*, the last figure denotes the coagulation concentration.

TABLE I

Chlorine displaced from $Fe(OH)_3$ sol when $N/10$-KIO_3 is added to it.

$N/10$-KIO_3 added.	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[IO_3] \times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·50	0·0981	1·74	1·79	0·21	5·00
1·00	0·0943	2·02	2·10	0·52	10·00
1·50	0·0916	2·24	2·38	0·75	15·00
2·00	0·0890	2·48	2·60	1·02	20·00
2·50	0·0855	2·84	2·99	1·41	25·00
3·00	0·0831	3·12	3·30	1·72	30·00

TABLE II

Chlorine displaced from $Fe(OH)_3$ sol when $N/50$-K_2SO_4 is added to it.

$N/50$-K_2SO_4 added.	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[SO_4] \times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·50	0·0922	2·19	2·28	0·70	1·00
1·00	0·0863	2·76	2·89	1·31	2·00
1·50	0·0838	3·04	3·20	1·61	3·00
2·00	0·0805	3·45	3·65	2·07	4·00
2·50	0·0736	4·52	4·81	3·23	5·00
3·00	0·0697	5·26	5·63	4·05	6·00

TABLE III

Chlorine displaced from $Fe(OH)_3$ sol when $N/200$-K-citrate is added.

$N/200$-K-citrate added.	π	$\alpha Cl. \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to [Citrate] $\times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
1·00	0·0985	1·72	1·76	0·18	0·50
2·00	0·0965	1·85	1·91	0·33	1·00
3·00	0·0935	2·08	2·15	0·57	1·50
4·00	0·0885	2·58	2·63	1·05	2·00
4·50	0·0825	3·20	3·33	1·75	2·25
5·00	0·0755	4·20	4·44	2·86	2·50

TABLE IV

Chlorine displaced from $Fe(OH)_3$ sol on adding $N/50$-K_2SO_4 + $N/10$-KIO_3.

0·5 c.c. K_2SO_4 + KIO_3	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to [SO_4] & [IO_3] $\times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·25	0·0941	2·03	2·10	0·52	3·50
0·50	0·0894	2·44	2·53	0·95	6·00
1·00	0·0845	2·96	3·08	1·50	11·00
1·50	0·0809	3·40	3·56	1·98	16·00
1·75	0·0785	3·73	3·92	2·34	18·50
2·00	0·0768	3·99	4·21	2·63	21·00

TABLE V

Chlorine displaced from $Fe(OH)_3$ sol on adding $N/200$-K-cit. + $N/10$-KIO_3.

1 c.c. K-Citr + KIO_3	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to [Citr]. & [IO_3] $\times 10^3$
0·00 c.c.	0·1012 volts,	1·54	1·58	0·00	0·00
0·25	0·0957	1·91	1·97	0·39	3·00
0·50	0·0934	2·09	2·16	0·58	5·50
1·00	0·0907	2·32	2·40	0·82	10·50
1·50	0·0862	2·77	2·88	1·30	15·50
2·00	0·0844	2·97	3·08	1·50	20·50
2·50	0·0772	3·93	4·12	2·54	25·50

TABLE VI

Chlorine displaced from $Fe(OH)_3$ sol on adding $N/10$-KIO_3 + $N/50$-K_2SO_4.

1 c.c. KIO_3 + K_2SO_4	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to [IO_3] & [SO_4] $\times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·10	0·0928	2·14	2·23	0·65	10·20
0·20	0·0856	2·88	2·97	1·39	10·40
0·40	0·0807	3·43	3·63	2·05	10·80
0·60	0·0756	4·18	4·41	2·83	11·20
0·80	0·0704	5·12	5·48	3·90	11·60
1·00	0·0628	6·84	7·44	5·86	12·00

TABLE VII

Chlorine displaced from $Fe(OH)_3$ sol on adding $N/200$-K-cit.$+N/50$-K_2SO_4.

0.5 c.c. K-citr $+K_2SO_4$	π	$\alpha Cl\times 10^3$	Total $[Cl]\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to [Citr] & $[SO_4]\times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·10	0·0986	1·71	1·76	0·18	0·45
0·30	0·0968	1·83	1·89	0·31	0·85
0·60	0·0921	2·20	2·29	0·71	1·45
0·90	0·0868	2·71	2·81	1·23	2·05
1·20	0·0820	3·26	3·45	1·87	2·65
1·50	0·0759	4·13	4·40	2·82	3·25

TABLE VIII

Chlorine displaced from $Fe(OH)_3$ sol on adding $N/10$-$KIO_3+N/200$-K-cit.

1 c.c. KIO_3 +K-cit.	π	$\alpha Cl\times 10^3$	Total $[Cl]\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[SO_4$ & $[Cit]\times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·50	0·0914	2·26	2·36	0·78	10·25
1·00	0·0842	2·99	3·15	1·57	10·50
2·00	0·0827	3·17	3·35	1·77	11·00
2·50	0·0806	3·44	3·65	2·07	11·25
3·00	0·0775	3·88	4·13	2·65	11·50
4·00	0·0753	4·23	4·51	2·93	12·00

TABLE IX

Chlorine displaced from $Fe(OH)_3$ sol on adding $N/50$-$K_2SO_4+N/200$-K-citrate.

0·5 c.c. K_2SO_4 +K-citr.	π	$\alpha Cl\times 10^3$	Total $[Cl]\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[SO_4]$ & [Cit]. $\times 10^3$
0·00 c.c.	0·1012 volts	1·54	1·58	0·00	0·00
0·50	0·0932	2·11	2·18	0·60	1·25
1·00	0·0888	2·52	2·62	1·04	1·50
2·00	0·0867	2·72	2·83	1·25	2·00
2·50	0·0852	2·88	3·02	1·44	2·25
3·00	0·0841	3·00	3·13	1·55	2·50
4·00	0·0810	3·39	3·55	1·97	3·00

DISCUSSIONS.

From the above results the following tables have been calculated.

Concentration of $Fe(OH)_3$ sol, as Fe_2O_3 = 9·018 g/litre.

Chlorine content of the sol = 0·012 g. ion/litre.

Purity of the sol i.e., Fe_2O_3/Cl = 751·0.

TABLE X

Displacement of chlorine ions from $Fe(OH)_3$ sol by ions of different valency.

Electrolyte added.	Displacement of [Cl] ions from $Fe(OH)_3$ sol $\times 10^3$.	[Cl] equiv. to electrolyte added $\times 10^3$.	Electrolyte added.	Displacement of [Cl] ions from $Fe(OH)_3$ sol $\times 10^3$.	[Cl] equiv. to electrolyte added $\times 10^3$.	Electrolyte added.	Displacement of [Cl] ions from $Fe(OH)_3$ sol. $\times 10^3$.	[Cl] equiv to electrolyte added $\times 10^3$
	$N/10$-KIO_3			$N/50$-K_2SO_4			$N/200$-K-citrate	
0·50 c.c.	0·21	5·00	0·50 c.c.	0·70	1·00	0·50 c.c.	0·18	0·50
1·00	0·52	10·00	1·00	1·31	2·00	1·00	0·33	1·00
1·50	0·75	15·00	1·50	1·61	3·00	1·50	0·57	1·50
2·00	1·02	20·00	2·00	2·07	4·00	2·00	1·05	2·00
2·50	1·41	25·00	2·25	3·23	4·50	2·25	1·75	2·25
3·00	1·72	30·00	2·50	4·05	5·00	2·50	2·86	2·50

From the above table it will be seen that the amount of chlorine displaced in the case of ferric hydroxide sol increases with K_2SO_4 as compared to KIO_3, and then again decreases with K-citrate. This can be explained on the basis of the purity of the sol. We have observed previously that with these sols there is always a certain purity after which chlorine ions released is less than the equivalent of the added electrolyte, whereas with less pure sols the released chlorine is greater than the added electrolyte. The ferric hydroxide sol is purer than this limit.

A result similar to the one observed here was obtained by Weiser (*J. Phys. Chem.*, 1931, 35, 9) with ferric hydroxide sol, using KNO_3, K_2SO_4, K-citrate and $K_3Fe(CN)_6$. In his case also, with uni-univalent electrolyte the displaced chlorine was the lowest, then it suddenly increased when K_2SO_4 was used and decreased again in the case of K-citrate and $K_3Fe(CN)_6$. In Weiser's case also, a similar effect is noticed as $Fe(OH)_3$ was purer than the limiting stage. The two results are summarised in the following table.

TABLE XI

Concentration of Weiser's sol = 6·46 g./litre.
Chlorine content = 0·0158 g. ions/litre.
Purity of Weiser's sol = 408·7.

Concentration of author's sol = 9·018 g./litre.
Chlorine content = 0·012 g. ions/litre.
Purity of author's sol = 751·0.

Electrolytes used.	Displacement of [Cl] × 10^3 from sol used by Weiser.	Displacement of [Cl] × 10^3 from sol used by author.
KNO_3	...	...
KIO_3	...	1·72
K_2SO_4	4·67	4·05
K-citrate	4·10	2·86
$K_3Fe(CN)_6$	3·17	...

From the results recorded in Tables IV-IX, the following tables have been calculated in which the release of chlorine ions as observed and calculated when adding one electrolyte in presence of another is given. The theoretical release due to the combined effect of both the electrolytes has also been calculated and given in columns 2 and 5 of the following tables.

TABLE XII

Displacement of chlorine ions from $Fe(OH)_3$ sol when $N/50$-K_2SO_4 + $N/10$-KIO_3 and $N/200$-K-citrate + $N/10$-KIO_3 are added to it in pairs.

0·5 c.c. K_2SO_4 + c.c. of KIO_3.	Calc.	Obs	1 c.c. K-citr. + c.c. of KIO_3.	Calc.	Obs.	[Cl] eqvt. to electrolyte added.
0·25	0·80	0·52	0·25	0·28	0·39	3·50
0·50	0·91	0·95	0·50	0·39	0·58	6·00
1·00	1·22	1·50	1·00	0·70	0·82	11·00
1·50	1·45	1·98	1·50	0·93	1·30	16·00
1·75	1·60	2·84	...	.	...	18·50
2·00	2·70	2·63	2·00	1·20	1·50	21·00
2·50	...	...	2·50	1·59	2·51	26·00

TABLE XIII

Displacement of chlorine ions from $Fe(OH)_3$ sol when $N/10$-KIO_3+$N/50$-K_2SO_4 and $N/10$-KIO_3+$N/200$-K-citrate are added in pairs to it.

1 c.c. KIO_3 + c.c. of K_2SO_4.	Calc.	Obs.	1 c.c. KIO_3 + c.c. K-citr.	Calc.	Obs.	[Cl] eqvt. to electrolyte added × 10^3.
0·10	0·67	0·65	...	...	...	10·20
...	...	...	0·25	0·62	0·78	10·25
0·20	0·82	1 39	...	...	...	10·40
...	...	...	0·50	0·70	1·57	10·50
0·40	1·04	2·05	...	...	...	10·80
...	...	...	1·00	0·85	1·77	11·00
0·60	1·32	2·83	...	...	...	11·20
...	...	...	1·25	0·97	2·07	11·25
...	...	...	1·50	1·09	2·65	11·50
0 80	1·62	3 90	...	...	...	11·60
1·00	1·83	5·86	2·00	1·57	2·93	12·00

TABLE XIV

Displacement of chlorine ions from $Fe(OH)_3$ sol when $N/200$-K-citrate+$N/50$-K_2SO_4 and $N/50$-K_2SO_4+$N/200$-K-citrate are added in pairs to it.

1 c.c. K-citr. + c.c. K_2SO_4	Calc.	Obs.	1 c.c. K_2SO_4 + c.c. K-citr.	Calc.	Obs.	Cl] eqvt. to electrolyte added × 10^3.
0·10	0·25	0·18	...	...	...	1·20
0·30	0·50	0·31	...	...	...	1·60
0·60	0·90	0·71	...	...	...	2·20
...	...	...	0·25	0·80	0·60	2·25
...	...	...	0·50	0·88	1·04	2·50
0·90	1·27	1·23	...	...	...	2·80
1·00	3 77	3·32	1·00	1·03	1·25	3·00
...	...	...	1·25	1·12	1·44	3·25
1·20	1·55	1·87	...	...	...	3·40
...	...	...	1·50	1·27	1·55	3·50
1·50	0·71	2·82	2·00	1·75	1·97	4·00

From the above results we find that with ferric hydroxide sol, in almost all cases, amount of released chlorine is greater than the calculated value. This means that the mixture induces more instability than the combined effects of the two electrolytes when taken in singles. A necessary consequence of this is that there should be no positive ionic antagonism *i.e.*, the amount of electrolyte necessary to coagulate should be less than than the additive. This has been observed by previous workers with these sols but with other pairs of electrolytes.

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CHARGE AND STABILITY OF COLLOIDS. PART X. STUDIES ON THE RELEASE OF COUNTER IONS FROM Cr (OH) SOL ON THE ADDITION OF PAIRS OF ELECTROLYTES

By B. P. Yadava

The effect of the addition of pairs of electrolytes on release of counter ions from Cr $(OH)_3$ sol, has been studied. It has been found that in almost all cases the amount of released chlorine is greater than the calculated value. This means that the mixture induces more instability a necessary consequence of which is that there should be no ionic antagonism.

In the previous communication of this series (p. 357) the effect of adding pairs of electrolytes to $Fe(OH)_3$ sol, has been studied. In this paper it has been endeavoured to show the effect of the same pairs of electrolytes with Cr $(OH)_3$ sol under similar conditions in order to find out if this sol also behaves similar to the ferric hydroxide sol.

Experimental

The sol of chromium hydroxide was prepared by the method given in a previous paper of this series (*J. Indian Chem. Soc.*, 1943, 20, 219). The method of procedure was the same as in the previous communication with Fe $(OH)_3$ sol.

Table I

Chlorine displaced from $Cr(OH)_3$ sol on adding N/10-KIO_3.

KIO_3 added to sol.	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[IO_3]$ $\times 10^3$
0·00 c.c.	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0502	11·25	12·41	1·16	5·00
1·00	0·0488	11·87	13·12	1·87	10·00
2·00	0·0476	12·44	13·76	2·51	20·00
3·00	0·0465	12·98	14·37	3·12	30·00
4·00	0·0441	14·26	15·86	4·61	40·00
5·00	0·0413	15·90	17·72	6·47	50·00

Table II

Chlorine displaced from Cr $(OH)_3$ sol on adding N/50-K_2SO_4.

K_2SO_4 added to sol.	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[SO_4]$ added $\times 10^3$
0·00 c.c.	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0506	11·07	12·20	0·95	1·00
1·00	0·0487	11·92	13·16	1·91	2·00
1·50	0·0451	13·71	15·22	3·97	3·00
2·00	0·0434	14·65	16·30	5·05	4·00
2·50	0·0424	15·23	16·97	5·72	5·00
3·00	0·0414	15·83	17·67	6·42	6·00

TABLE III

Chlorine displaced from $Cr(OH)_3$ sol on adding *N*/100-K-citrate to it.

K-cit. added to sol.	π	$\alpha Cl \times 10^3$	Total [Cl] × 10^3	[Cl] displ. × 10^3	[Cl] eqvt. to [Cit] added × 10^3
0·00 c.c.	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0502	11·20	12·36	1·11	0·50
1·00	0·0488	11·87	13·11	1·86	1·00
2·00	0·0469	12·78	14·15	2·60	2·00
3·00	0·0542	13·66	15·14	3·89	3·00
4·00	0·0436	14·53	16·15	4·90	4·00
5·00	0·0423	15·29	17·03	5·78	5·00

TABLE IV

Chlorine displaced from $Cr(OH)_3$ sol on adding *N*/50-K_2SO_4+*N*/10-KIO_3.

0·5 c.c. K_2SO_4+ c.c. of KIO_3.	π.	$\alpha Cl \times 10^3$.	Total [Cl] × 10^3	[Cl] displ. × 10^3	[Cl] eqvt. to [SO_4] & [IO_3] × 10^3
0·00	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0492	11·68	12·90	1·65	7·00
1·00	0·0468	12·84	14·21	2·96	12·00
1·50	0·0443	14·15	15·75	4·50	17·00
2·00	0·0425	15·17	16·92	5·67	22·00
2·50	0·0414	15·83	17·69	6·44	27·00
3·00	0·0405	16·40	18·35	7·10	32·00

TABLE V

Chlorine displaced from $Cr(OH)_3$ sol on adding *N*/100-K-citr.+*N*/10-KIO_3.

1 c.c. K-citr.+ c.c. of KIO_3	π	$\alpha Cl \times 10^3$	Total [Cl] × 10^3	[Cl displ. × 10^3	[Cl] eqvt. to [Cit.] & [IO_3] added × 10_3
0·00	0·0527 volts	10·20	11·25	0·00	0·00
1·00	0·0496	11·51	12·70	1·45	11·00
1·50	0·0480	12·25	13·53	2·28	16·00
2·00	0·0472	12·64	13·97	2·72	21·00
2·50	0·0457	13·39	14·85	3·60	26·00
3·00	0·0440	14·31	15·91	4·66	31·00
3·50	0·0427	15·05	16·76	5·51	36·00

TABLE VI

Chlorine displaced from $Cr(OH)_3$ sol on adding $N/10$-KIO_3 + $N/50$-K_2SO_4.

1 c.c. of KIO_3 + c.c. K_2SO_4	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[IO_3]$ & $[SO_4]$ $\times 10^3$
0·00	0·0527 volts	10·20	11·25	0·00	0·00
0·25	0·0485	12·01	13·27	2·02	10·50
0·50	0·0449	13·82	15·35	4·10	11·00
1·00	0·0425	15·17	16·91	5·66	12·00
1·50	0·0399	16·79	18·78	7·53	13·00
2·00	0·0373	18·57	20·84	9·59	14·00
3·00	0·0335	21·55	24·41	13·16	16·00

TABLE VII

Chlorine displaced from $Cr(OH)_3$ sol on adding $N/100$-K-citrate + $N/50$-K_2SO_4.

1 c.c. K-cit + c.c. K_2SO_4	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to [Cit] & $[SO_4] \times 10^3$
0·00	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0475	12·49	13·80	2·55	2·00
1·00	0·0455	13·49	14·97	3·32	3·00
1·50	0·0440	14·31	15·91	4·66	4·00
2·00	0·0433	14·70	16·36	5·11	5·00
2·50	0·0423	15·29	17·05	5·80	6·00
3·00	0·0413	15·90	17·74	6·49	7·00

TABLE VIII

Chlorine displaced from $Cr(OH)_3$ on adding $N/10$-KIO_3 + $N/100$-K-citrate.

1 c.c. KIO_3 + c.c. of K-cit.	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt. to $[IO_3]$ & [Cit] $\times 10^3$
0·00	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0478	12·34	13·65	2·40	10·50
1·00	0·0442	14·20	15·78	4·53	11·00
2·00	0·0435	14·59	16·23	4·98	12·0
2·50	0·0424	15·23	16·95	5·70	12·50
3·00	0·0409	16·15	18·08	6·77	13·00
4·00	0·0398	16·85	18·65	7·60	14·00

TABLE IX

Chlorine displaced from $Cr(OH)_3$ sol on adding $N/50$-K_2SO_4 + $N/100$-K-citrate.

1 c.c. of K_2SO_4 + c.c. K-cit.	π	$\alpha Cl \times 10^3$	Total [Cl] $\times 10^3$	[Cl] displ. $\times 10^3$	[Cl] eqvt to $[SO_4]$ & [Cit]. $\times 10^3$
0·00	0·0527 volts	10·20	11·25	0·00	0·00
0·50	0·0464	13·03	14·48	3·23	2·50
1·00	0·0448	13·87	15·45	4·20	3·00
1·50	0·0431	14·82	16·52	5·27	3·50
2·00	0·0418	15·59	17·40	6·15	4·00
3·00	0·0402	16·60	18·54	7·29	5·00
4·00	0·0389	17·46	19·53	8·28	6·00

DISCUSSION

From the above results the following tables have been calculated.

Concentration of Cr $(OH)_3$ sol, as Cr_2O_3 = 8·88 g. per litre.

Chlorine content of the sol = 0·054 g. per litre.

Purity of the sol *i.e.*, Cr_2O_3/Cl = 127.

TABLE X

Displacement of chlorine ions from chromium hydroxide sol.

Electrolyte added	Displacement of [Cl] from the sol	[Chlorine] equiv. of the electrolyte added	Electrolyte added	Displacement of [Cl] from the sol	[Chlorine] equiv. of the electrolyte added	Electrolyte added	Displacement of [Cl] from the sol	[Chlorine] equiv. of the electrolyte added
$N/10$-KIO_3			$N/50$-K_2SO_4			$N/100$-K-citrate		
0·50 c.c.	1·16	5·00	0·50 c.c.	0·95	1·00	0·50 c.c.	1·11	0·50
1·00	1·87	10·00	1·00	1·91	2·00	1·00	1·86	1·00
2·00	2·51	20·00	1·50	3·97	3·00	2·00	2·60	2·00
3·00	3·12	30·00	2·00	5·05	4·00	3·00	3·89	3·00
4·00	4·61	40·00	2·25	5·78	4·50	4·00	4·90	4·00
5·00	6·47	50·00	3·00	6·42	6·00	5·00	5·78	5·00

From the above table it will be seen that with chromium hydroxide sol the displacement of chlorine ions is almost the same with all the electrolytes. This can explained on the basis of the purity of the sol. It has been observed previously that with these sols there is always a certain purity below which chlorine ions released is always

less than the equivalent of the added electrolyte, whereas with less pure sols the released chlorine is greater than the added electrolyte. The ferric hodroxide sol in previous paper is purer than this limit, but here the $Cr(CH)_3$ sol is less pure.

In the case of Cr $(OH)_3$ sol it is observed that the quantity of chlorine ions released at the coagulation concentration is approximately the same. This peculiar behaviour is connected with the impure nature of $Cr(OH)_3$ sol.

From the results recorded in Tables I—IX, the following tables have been calculated in which the release of the chlorine ions as observed and calculated when adding one electrolyte in presence of another is given. The theoretical release due to the combined effect of botn the electrolytes has also been calculated and given in columns 2 and 5 of the following tables

TABLE XI

Displacement of Cl ions from Cr $(OH)_3$ sol when $N/50$-K_2SO_4+$N/10$-KIO_3 and $N/100$-K-citrate+$N/10$-KIO_3 are added to it in pairs.

0·5 c.c. K_2SO_4 +c.c. of KIO_3	Calc.	Obs.	1 c.c. K-citr.+ c.c. of KIO_3	Calc.	Obs.	[Cl] eqvt. to electrolyte added $\times 10^3$
0·50	2·11	1·65	...	...	...	6·00
1·00	2·82	2·96	1·00	3·73	1·45	11·00
1·50	3·15	4·50	1·50	4·06	2·28	16·00
2·00	3·46	5·67	2·00	4·37	2·72	21·00
2·50	3·78	6·44	2·50	4·68	3·60	26·00
3·00	4·07	7·10	3·00	4·98	4·66	31·00
3·50	...	...	3·50	5·66	5·51	36·00

TABLE XII

Displacement of Cl ions from Cr $(OH)_3$ sol when $N/10$-KIO_3+$N/50$-K_2SO_4 and $N/10$-KIO_3+$N/100$-K-citrate are added to it in pairs.

1 c.c. KIO_3+ c.c. of K_2SO_4	Calc.	Obs.	1 c.c. KIO_3+ c.c. K-cit.	Calc.	Obs.	[Cl] eqvt. to electrolyte added $\times 10^3$
0·25	2·37	2·02	0·50	2·98	2·40	10·50
0·50	2·82	4·10	1·00	3·73	4·53	11·00
1·00	3·78	5·65	2·00	4·47	4·98	12·00
...	...	...	2·50	5·00	5·70	12·50
1·50	5·84	7·53	3·00	5·76	6·77	13·00
2·00	6·92	9·59	4·00	6·77	7·60	14·00
3·00	8·29	13·16	...	...	...	16·00

TABLE XIII

Displacement of Cl ions from $Cr(OH)_3$ sol when $N/100$-K-citrate+$N/50$-K_2SO_4 and $N/50$-K_2SO_4+$N/100$-K-citrate are added to it in pairs.

1 c.c. K-citr.+ c.c. K_2SO_4	Theor.	Obs.	1 c.c. K_2SO_4+ c.c. of K-cit.	Theor.	Obs.	[Cl] eqvt. to electrolyte added $\times 10^3$
0·50	2·81	2·55	...	...	...	2·60
...	...	...	0·50	2·06	3·23	2·50
1·00	3·77	3·32	1·00	2·82	4·20	3·00
...	...	...	1·50	3·23	5·27	3·50
1·50	5·83	4·66	2·00	3·55	6·15	4·00
...	...	...	3·00	4·84	7·29	5·00
...	...	...	4·00	5·85	8·28	6·00

From the above results it is found that with chromium hydroxide sol as well, the amount of released chlorine is greater than the calculated value. This means that the mixture induces more instability than the combined effects of the two electrolytes when taken in singles. A necessary consequence of this is that there should be no positive ionic antagonism i.e., the amount of electrolyte necessary to coagulate, should be less than the additive. This has been observed by previous workers with these sols, but with other pairs of electrolytes.

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METHODS FOR THE DETERMINATION OF TRACE ELEMENTS IN SOILS AND PLANTS. PART I. DETERMINATION OF BORON AND MANGANESE

By V. V. K. Sastry and B. Viswanath

A new method has been described for the estimation of small amounts of boron (4 ppm) and Mn (80 ppm) in soils and plant samples.

It is now fairly well established that the presence of at least some of the minor elements in the soil is essential for normal plant growth. Such trace elements as boron, manganese, copper and zinc are necessary for the completion of the vegetative cycle of certain plants. It has, therefore, become necessary to develop and perfect the methods of analysis for the estimation of these elements in Indian soils and plant materials.

Methods in use. (a) *Spectrographic methods* :—Though accurate for the estimation of metallic trace elements up to 1 p. p. m. they are not widely popular on account of the elaborate equipment, expense and the training required in execution.

(b) *Colorimetric micro-chemical methods* :—Though at times tedious, particularly when estimating a number of trace elements in a series of samples, these are largely favoured on account of the ease of manipulation.

The present investigation was taken up in connection with the soil survey experiments conducted by this Institute and the methods for the estimation of boron, and manganese have been tested and standardised by examining the recoveries of varying amounts of added boron and manganese from six soil samples.

Experimental

Double distilled water was used throughout the work.

(a) *Preparation of soil sample.*—Finely powered soil (2g.) was intimately mixed with 10g. of pure anhydrous sodium carbonate and fused in a platinum dish. After cooling it was placed in a 250 c.c. beaker containing 25 c.c. of distilled water. The contents were warmed after adding 10 c.c. of $4N$ sulphuric acid and covered with a clock glass. The addition of acid in 10 c.c. lots was continued until the melt had completely disintegrated and the residues had become colourless. The resulting solution and the washings were filtered into a 100 c.c. flask and made up to 100 c.c. after cooling. This formed the starting solution for the estimation of boron and manganese in the soil.

(b) *Examination of plant material for Boron and Manganese.*—To detect the differences in the mineral content of healthy and diseased plant materials the spectrographist solves the problem by incinerating the two samples under identical conditions and by comparing the two spectrograms, line by line, to detect any difference in the intensities of the two corresponding lines. They may later on be measured by microphotometry to get the absolute values for the two lines.

The micro-analyst ashes the samples under identical conditions, dissolves them in acid to a known volume and estimates the elements in question in aliquots. Work. of this type has been carried out on healthy and various infected samples of tobacco leaf and the results are reproduced below.

Determination of Boron

The increasing use of boron as a fertiliser and the recognition of physiological disorders in plants due to boron deficiencies have resulted in the development of a number of methods for its estimation in soils and plant materials. Wilcox has applied the electrometric titration method for the purpose in the case of the soils and plants of the arid or semi-arid regions of the west where the boron concentration is fairly high. In the more humid regions with a lower concentration of boron, spectroscopic and the quinalizarin methods are in general use. Recently Neelakantam and Rangaswamy (*Proc. Ind. Acad. Sci.*, 1943, **18A**, 171) have reported a new colorimetric method for the estimation of boron in pure solutions depending on the yellow coloration obtained by boric acid with pentamethyl-quercetin in presence of citric acid in anhydrous acetone medium. It is proposed to test this method in respect of soil and plant materials when a sufficient quantity of the reagent is available.

Of the several hydroxy-anthraquinones which have the property of changing colour when boron is added in concentrated sulphuric acid medium, quinalizarin has been found to be the most suitable, the colour changing from violet to blue with increasing concentration of boron. The colour is destroyed by oxidising agents and the sensitivity of the test depends upon the concentration of sulphuric acid, the final concentration of 93% being found most satisfactory. The method of Smith (*Analyst*, 1935, **60**, 735) consists in pipetting 1 c.c. of the unknown or the standard solution into a graduated tube containing exactly 9 c.c. of 98·5% sulphuric acid. After thorough mixing and cooling, 0·5 c.c. of the quinalizarin solution (10 mg. in 100 c.c. of 93% sulphuric acid) is added and allowed to stand for 15 minutes and the unknowns are compared against standards prepared in exactly the same way.

Suitable colour standards have not yet been developed for this reaction. Hence a standard curve with varying amounts of boron (0·002 to 0·016 mg. per c.c.) compared with a blank, containing only distilled water as an index of concentration has been prepared employing the percentage of light transmission for the purpose. With this standard curve a secondary curve has been drawn for boron concentration varying from 0·0002 to 0·001 mg. per c.c.

It is necessary to use for fusion a large proportion of sodium carbonate for estimating the total boron content in the soil. It is advantageous to add sulphuric acid to the water for extracting the melt. Since the same solution was used to estimate manganese also, the melt was extracted with acid and addition of alcohol up to 70% by volume throws down most of the sodium sulphate formed. It is necessary to ignite the residue after the final evaporation to destroy any volatile organic matter present in the alcohol.

The technique of the colorimetric method using quinalizarin as perfected by Olson and DeTurke (*Soil Sci.*, 1940, **50**, 257) has been adapted to Indian soils with a

few alterations in a Pulfrich photometer and all the reagents were prepared according to the instructions of Berger and Truog. The soil solution (25 c.c. containing 5g. of the soil) was pipetted into a conical flask, shaken with 150 c.c. of 95% ethyl alcohol and the supernatant liquid filtered into a 500 c.c. conical flask. After addition of 100 c.c. of distilled water to prevent subsequent precipitation and of potassium carbonate to make it just alkaline, the alcohol was distilled off to a small volume. The contents were then transferred to a platinum dish, evaporated to dryness and ignited. The residue was triturated with 5 c.c. of 0·36 *N*-sulphuric acid and transferred along with the washings of the dish to a 50 c.c. measuring flask and made up to the mark after cooling.

This solution (5 c.c.) was placed in a Nessler's tube, mixed with 45 c.c. of sulphuric acid (98·5%) and cooled. After adding 2·5 c.c. of 0·01% solution of quinalizarin the tube was lightly corked and allowed to stand at room temperature for at least 30 minutes. The intensity of the colour developed—(red-violet or blue-violet) was matched against a blank containing 5 c.c. of distilled water in place of the test solution. The percentage light transmissibility was measured in a Pulfrich photometer by placing the solutions in comparison vessels (30·11 cm. long)

The aperture of the photometer on the solution side was completely opened and the drum on the other side adjusted till an equal illuminaiion was obtained through the light blue filter (L 3-37). The difference between the two drum readings gives the percentage of light cut down by the test solution when viewed through the light blue filter which is directly proportional to the concentration of boron. The amount of boron present in the reagents is subtracted from this value to get the total boron content of the soil. All the data in the tables have been approximated to the nearest integer.

TABLE I

Sample.	Serial No.	Conc. of boron in p. p. m. in soil.	added.	recovered.
Surface soil (0-6″) from Kalshakaka (Punjab)	599	28	50 100 150	48 97 146
Soil profile (0-1′) from Gurdaspur (Punjab)	592	68	100 200 300 320	96 198 296 316
Soil profile (0-1′) from Lahore (Punjab) Virgin soil.	564	66	420 520	415 516
Soil profile (0-1′) from Kangra (Punjab)	585	86	200 250 300	197 246 297
Surface soil (0-9″) from Burn's Garden (Karachi-Sind)	604	29	150 225 300	147 221 296
Soil profile (0-1′) from Malir farm, Karachi (Sind) ...	608	32	225 200	223 198
Blank for reagents.		0·2	275	271

Determination of Boron in healthy and Virus-infected samples of Tobacco.—Finely powdered plant material (2g.) was oven dried and ashed in a platinum dish. The ash was triturated with 5 c.c. of 3·6 *N*-sulphuric acid and filtered and washed into 100

c.c. measuring flask and made up to the volume after cooling. A 25 c.c. aliquot of this solution were evaporated nearly to dryness, redissolved in 20 to 25 c.c. of 0·36 *N*-sulphuric acid and made up to 50 c c. 5 c.c. aliquots of this formed the test solutions. The details of further procedure were as described above in respect of soils with this difference that the experiments were conducted in duplicate as no recoveries were tested in their case. The results of analysis in duplicate of six samples of tobacco are given below.

TABLE II

Sample	Serial No.	Conc of boron in P. P. M. Expt. 1	Expt. 2.
I. P. H. 142-Healthy	795 of 1942	15	14
-do- Diseased	796 of 1941	20	20
Harissons Special-Healthy	797 of „	11	11
-do- Diseased	798 of „	13	13
I. P. H. 142-Healthy	183 of 1942	11	11
-do- Diseased	184 of „	11	11

Determination of Manganese in Soils.

Both micro and macro-methods have been in use for the estimation of manganese in soils, rocks and plants. The official gravimetric and volumetric methods recommonded by the A. O. A. C, (1925 and 1930) are not, however, very popular and micro methods, for which elaborate technique has been developed, are in general use.

The colorimetric method of estimating manganese by oxidising the manganese salts to permanganate in strongly acid media with persulphates, periodates and peroxides of lead, bismuth etc., was adopted by a number of workers but with conflicting results depending on the particular oxidising agents employed. The pink colour developed in the reaction is matched against a standard of known manganese content.

Willard Greathouse (*J. Amer. Chem. Soc.*, 1917, **39**, 2366) were the first to establish the accuracy of the periodate method for the quantitative determination of manganese. This method has been successfully applied by different investigators, to water, animal and vegetable tissues, rocks and soils and salt solutions. A thorough spectrophotometric study of the method with special attention to the effect of the presence of other ions in the colour system has been made by Mehling (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 274) who established that, though the presence of a few of the 56 common ions interfere with the colour, the colour is stable for over two months and follows Beer's law. The production of colour is also independent of the presence of varying amounts of sulphuric acid, nitric and phosphoric acids or periodates.

Preparation of Mn Standard.—A stock solution of $N/50$-$KMnO_4$ is prepared by weighing the exact amount of the pure salt into a liter flask, dissolving and making up the solution to 1000 c.c. It is then filtered through glass wool into a stoppered

dry amber coloured bottle and kept in the dark at least for four days before standardising it. The exact volume of *N*/50-$KMnO_4$ (158·15 c.c.) required to make one liter of the desired concentration (0·1 mg. per c c.) is taken in a litre flask, diluted with 100 c.c. of water before adding 20 c.c. of concentrated sulphuric acid. A solution of sodium bisulphite is slowly stirred into the mixture until the permanganate colour is just discharged. Any excess of sulphurous acid is oxidised by adding a few drops of concentrated nitric acid. After cooling the solution is made up to one litre.

Varying quantities of this solution were re-oxidised with phosphoric acid and sodium periodate and made up to 50 c.c. The colour of the resulting permanganate solution was compared with a blank carried out with distilled water and the reagents using light blue (L3-37) filter. The two solutions, standard and the blank, were placed in 10 c.c. comparison tubes with quartz faces and the maximum amount of light allowed to pass through the coloured standard. The drum on the side of the blank was adjusted till the intensity of light passing through the two tubes as viewed through the filter was the same. The reading on the drum was noted and repeated with the cells interchanged. The photometer difference was plotted against the concentration in mg. of $KMn.O_4$, in the total volume of the final solution (50 c.c.) for a series of standards and represented by a curve. Reagents required were concentrated sulphuric acid, concentrated nitric acid, phosphoric acid,—(*d*, 1·70) and sodium periodate (B. D. H. product).

(*a*) *Estimation of Manganese in soils.*—Soil extract (25 c.c.) after destroying the organic matter was taken in a silica crucible and heated on a water-bath with the addition of 5 c.c. of concentrated sulphuric acid to eliminate chlorides. At this stage 5 c.c. concentrated nitric acid followed by 1 c.c. of phosphoric acid were added and heated till all the nitrous fumes were driven off. To the mixture were added 20 c.c. of distilled water and 0·2 g. of sodium periodate and after careful boiling the resulting solution was kept undisturbed till the development of the pink colour was complete. After cooling the solution was made up to 50 c.c. Aliquots of this solution were taken in a 10 c.c. comparisan cell and matched with a blank containing water and the reagents as described above in a Pulfrich photometer. Known amounts of manganese were added and the recoveries measured in the case of 6 soils. The results are expressed in parts per million in terms of potassium permanganate.

The above experiments show that the ions usually present in soil do not interfere with the colour formation.

The procedure adopted by Willard and Greathouse was followed in producing the colour system.

TABLE III.

Sample	Serial No.	Conc. of Mn as KMnO4 in p p m. in soil	added	recovered
Surface soil (0-6′) from Kalshakaka (Punjab)	599	2700	2500 5000 7500	2550 5045 7550
Soil profile (0-1′) from Gurdaspur (Punjab)	592	3680	1000 1250 1500	1020 1275 1515
Soil profile (0-1′) from Lahore (Punjab) Virgin soil	564	2450	3000 3240 3500	3040 3275 3545
Soil profile (0-1′) from Kangra (Punjab)	585	4700	2000 2250 2500	2015 2275 2520
Surface soil (0-9″) from Burns Garden, (Sind)	604	4800	1500 1750 2000	1510 1740 1985
Soil profile (0-1′) from Malir farm, Karachi (Sind)	608	1360	1200 1700 2200	1220 1715 2240
Blank for reagents.		Nil		

Estimation of Manganese in healthy and virus infected samples of tobacco. The acid extract of the ash (25 c.c.) as prepared in the 6 cases for estimation of boron were taken in a silica crucible and the permanganate colour developed as described above. The experiments were conducted in duplicate for reproducibility and accuracy. The Mn content of six samples is given below.

TABLE IV.

Description Sample	Serial No.	Conc. of Mn in p. p. m. Expt. 1.	Expt. 2.
I. P. H. 142 Healthy	795 of 1941	139	137
Do. Diseased	796 of „	95	95
Harisson' special-Healthy	797 of „	100	100
Do. Diseased	798 of „	83	81
I. P. H. 142 Healthy	183 of 1942	70	72
Do Diseased	184 of „	78	79

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STUDIES IN THE SANTALOL SERIES. PART VII. ELECTROCHEMICAL PROPERTIES OF TERESANTALIC ACID AND TRICYCLOEKASANTALIC ACID

By P. C. Guha and S. C. Bhattacharyya

The electrochemical properties of teresantalic acid and *tricyclo*ekasantalic acid have been studied. It has been found that there is a direct relationship existing between steric hindrance and the strength of acids.

As a prelude to a systematic study of the different acids of the santalol series for determining the influence of ring structure on the general characteristics of the compounds, electrochemical properties of teresantalic acid and *tricyclo*ekasantalic acid (*vide infra* for formulae) have been studied. An interesting relationship existing between steric hindrance and ionisation constant observed in this connection has been discussed at the end of this paper. A drum-roller meter bridge was used in these experiments described in this connection.

Teresantalic acid was isolated from sandalwood oil according to the method of Soden and Muller (*Pharm. Z.*, 1899, **44**, 258) and was purified by fractional distillation under vacuum and then by crystallisation twice from petrol-ether; m.p. 157°; b.p. 127°/1 mm.; $[\alpha]_D = -76{\cdot}5°$ (in benzene).

Solubility.—A saturated solution of the substance in conductivity water was prepared by shaking an excess of the powdered acid in water for 48 hours and the amount of substance in solution was determined by conductometric titration with standard alkali as shown graphically in Fig. 1 (curve 1). Solubility calculated from the graph was $4{\cdot}9 \times 10^{-3}$ g. mol. per litre at 22·8°.

Mobility and absolute velocity of the anion were determined by measuring the conductivity of the sodium salt of the acid at different dilutions. The salt solution was prepared by adding the acid in a standard solution of alkali. To prevent hydrolysis a slight excess of the free acid was always kept in suspension. The data obtained are presented in Fig. 2 (curve 1) as equivalent conductivity against $\sqrt{C}$. Λ_∞ (as found from the graph) was 68·85 mho at 22·8°. This tallies fairly well with the value 69·26, obtained by calculation from the Kohlrausch's formula ($\Lambda_\infty = \Lambda_0 + b\sqrt{C}$). Therefore the mobility of the anion was $68{\cdot}85 - L_{Na} = 68{\cdot}85 - 48{\cdot}21 = 20{\cdot}64$. Hence the absolute velocity of the anion was $20{\cdot}64/96{,}500 = 21{\cdot}4 \times 10^{-5}$ cm./sec. at 22·8°.

Degree of Ionisation and Ionisation Constant.—The mean of several estimations of the specific conductivity of the saturated solution of the acid in conductivity water (specific conductivity $0{\cdot}68 \times 10^{-6}$ mho) at 22·8° was found to be $6{\cdot}54 \times 10^{-5}$ and subtracting the conductivity due to the solvent that of the acid is $(6{\cdot}536 \times 10^{-4} - 0{\cdot}68 \times 10^{-6}) = 6{\cdot}47 \times 10^{-5}$.

Hence its equivalent conductivity $\Lambda = \dfrac{6{\cdot}47 \times 10^{-5} \times 1000}{4{\cdot}9 \times 10^{-3}} = 13{\cdot}2$. Therefore, the degree of ionisation $\alpha = \Lambda/\Lambda_\infty = 13{\cdot}2/20{\cdot}64 + 337{\cdot}5\ (L_H) = 0{\cdot}0368$. Therefore the ionisation constant

$$k = \frac{\alpha^2 c}{1-\alpha} = \frac{(0{\cdot}0368)^2 \times 0{\cdot}0049}{1 - 0{\cdot}0368} = 0{\cdot}69 \times 10^{-5} \text{ at } 22{\cdot}8°.$$

Tricycloekasantalic acid was prepared by the oxidation of sandalwood oil with potassium permanganate according to the method of Semmler (*Ber.*, 1907, **40**, 1120). It was purified by crystallising once from alcohol and twice from petrol-ether, m.p. 76·4° (Semmler, m.p. 72°), $[\alpha]_{5780} = +15{\cdot}4°$ (in alcohol). The electrochemical properties of the acid and its salt were determined exactly as in the previous case.

Solubility.—Conductometric titration of the saturated solution of the acid in conductivity water has been shown graphically in Fig. 1 (curve 2). The solubility found from the graph $= 7{\cdot}1 \times 10^{-4}$ g. mol. per litre.

Mobility and Absolute Velocity of the Anion.—The equivalent conductivity of the sodium salt of the acid in presence of slight excess of suspended acid at different dilution was determined as previously and the relation between Λ and $\sqrt{C}$ has been shown in Fig. 2 (curve 2). Λ_∞ found from the graph $= 65{\cdot}35$ (from Kohlrausch's formula, $65{\cdot}01$). Therefore, the mobility of the anion $= 65{\cdot}35 - L_{Na} = 63{\cdot}35 - 48{\cdot}21 = 17{\cdot}14$. Hence the absolute velocity of the anion $= 17{\cdot}14/96{,}500 = 18{\cdot}3 \times 10^{-5}$ cm./sec. at $22{\cdot}8°$.

FIG. 1

Conductometric titration.

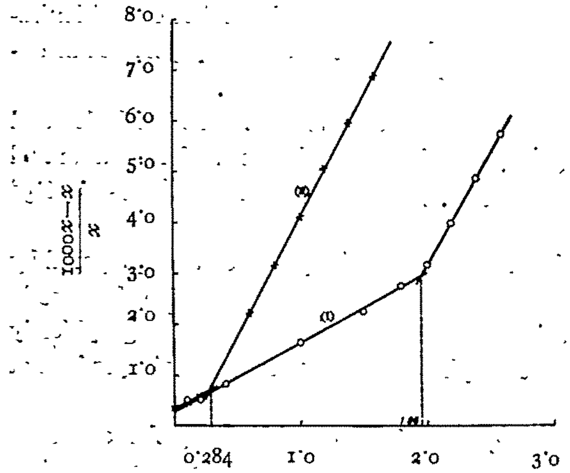
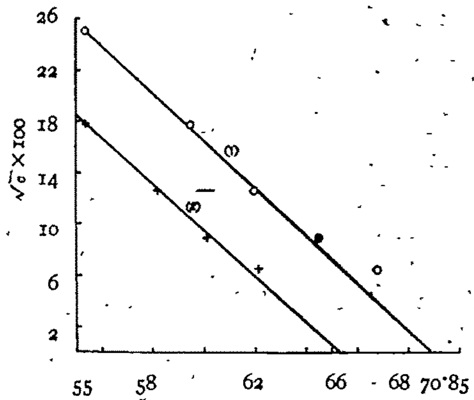


FIG. 2

Eq. conducty. against $\sqrt{c}$,



In figures curves 1 and 2 refer respectively to teresantalic acid and *tricyclo*ekasantalic acid.

Degree of Ionisation and Ionisation Constant.—The actual specific conductivity of the saturated solution of the acid was $3{\cdot}32 \times 10^{-5}$ mho (subtracting that of water). Therefore, the equivalent conductivity $= 3{\cdot}32 \times 10^{-5} \times 1000/0{\cdot}00071 = 46{\cdot}76$.

Hence the degree of ionisation

$$\alpha = \Lambda/\Lambda_\infty = \frac{46{\cdot}76}{L_a + L_H} = \frac{46{\cdot}76}{337{\cdot}5 + 17{\cdot}14} = 0{\cdot}132$$

and consequently the ionisation constant

$$k = \frac{\alpha^2 c}{1-\alpha} = \frac{(0{\cdot}132)^2 \times 0{\cdot}71 = 10^{-3}}{1 - 0{\cdot}132} = 1{\cdot}43 \times 10^{-5} \text{ at } 22{\cdot}8°.$$

DISCUSSION

There are, however, some notable peculiarities in the electrochemical behaviour of these two acids. From the formulae given below it will be clear that teresantalic acid (I) may be regarded to be a trisubstituted derivative of acetic acid (II), and *tricyclo*ekasantalic acid (III) that of butyric acid (IV). The ionisation constants of these acids and those of some other allied compounds have been compared below (International Critical Table, 1929, Vol. VI, p. 260-390). In the table R stands for the radical represented by Fig. 3.

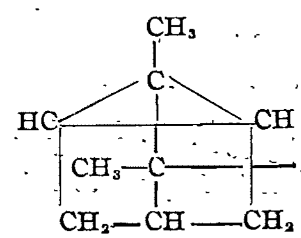


FIG. 3

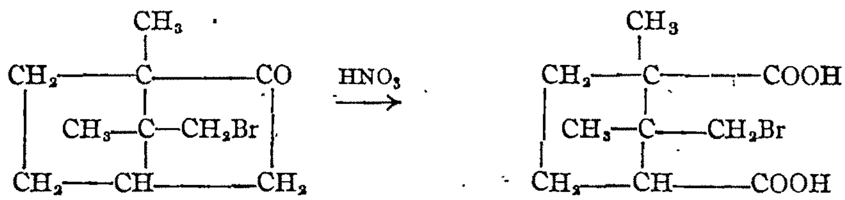
Name.	k.	Temp.	Name.	k.	Temp.
R-COOH Teresantalic acid (I)	$0·69 \times 10^{-5}$	22·8°	CH_3-CH_2-CH_2-CH_2-COOH Valeric acid (VI)	$1·56 \times 10^{-5}$	25
CH_3-COOH Acetic acid (II)	$1·813 \times 10^{-5}$	25			
R-CH_2-CH_2-COOH Tri*cyclo*ekasantalic acid (III)	$1·43 \times 10^{-5}$	22·8	$(CH_3)_2$CH-CH_2-COOH *iso*Valeric acid (VII)	$1·68 \times 10^{-5}$	25
CH_3 CH_2-CH_2-COOH Butyric acid (IV)	$1·5 \times 10^{-5}$	25			
CH_3—C(CH_3)$_2$—COOH Trimethylacetic acid (V)	$0·96 \times 10^{-5}$	25°	CH_3-CH_2—CH(CH_3)-COOH Methylethylacetic acid (VIII)	$1·67 \times 10^{-5}$	25

The ionisation constants of tri*cyclo*ekasantalic acid (III) and of butyric acid (IV) are nearly of the same order showing thereby that the heavy ring structure has no direct influence on the ionisation constant of the acid. The case is, however, entirely different with teresantalic acid (I). It being a lower homologue should ordinarily possess ahigher ionisation constant than that of tri*cyclo*ekasantalic acid, but the value actually found is only half of that of the latter. It appears, therefore, that in this case the proximity of the ring structure to the tertiary carboxyl group is exerting some dominating influence on the strength of the acid.

The above statement is supported by the following facts that the derivatives of teresantalic acid possessing identical ring structure, *viz*. teresantalol (R—CH_2OH) and teresantalyl chloride (R—CH_2Cl) though contain a primary hydroxyl group and a halogen atom exhibit great steric hindrance, as a result of which it is very difficult to make the hydroxyl group in teresantalol or the halogen atom in teresantalyl chloride to react.

In conformity with the above observations the following facts may also be cited. Among the ordinary fatty derivatives the tertiary compound trimethylacetic acid (V) is the nearest approach to teresantalic acid. Trimethylacetic acid (V) is, however, isomeric with valeric acid (VI), *iso*valeric acid (VII), methylethylacetic acid (VIII), but it possesses a much lower ionisation constant than the others, the ionisation constants of all of which are almost the same. It is already well known that esters of tertiary carboxylic acids like trimethylacetic acid show some resistance towards hydrolysis, the resistance of course decreasing when they are converted into the corresponding primary alcohols or halides. As already indicated teresantalic acid behaves rather differently, its steric hindrance obstinately persists in its derivatives teresantalol and teresantalyl chloride, both of which are not prone to ordinary chemical operations. It is noticeable that the ionisation constant of teresantalic acid is even lower than that of trimethylacetic acid. It is clear, therefore, that there is a direct relationship existing between steric hindrance and strength of acids. This, however, seems to have escaped the notice of earlier workers.

It is interesting to note that the bromine atom of π-bromocamphor (IX), though primary in character, is unusually inert. But when the π-bromocamphor is oxidised to the corresponding bromocamphoric acid (X), the ring undergoing fission, the inactivity of the bromine atom disappears absolutely, so much so, that it undergoes all ordinary chemical reactions with the greatest ease.



π-Bromocamphor (IX) — Bromocamphoric acid (X)

It is, therefore, probable that the carboxyl group in teresantalic acid is embedded in the ring structure in a peculiar way which hinders its ionisation and also shields it against outside influences. An X-ray examination of this and similar other compounds so as to determine the relative position and distances of the different atoms and atomic groupings will furnish interesting results. Further work for an exhaustive study of this point is in progress.

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ORTHO-SUBSTITUTED DIPHENYLS. PART II.

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o-Cyanodiphenyl has been hydrolysed to give *o*-phenylbenzoic acid with the formation of the *o*-phenylbenzamide as the intermediate product. A new method for the preparation of *o*-phenylbenzaldehyde has been described and the preparation of *o*-phenylcinnamic acid accomplished for the first time.

Kaiser (*Annalen*, 1890, **257**, 100) claimed to have prepared *o*-phenylbenzoic acid by the hydrolysis of *o*-diphenylnitrile with alcoholic potash. The hydrolysis of this nitrile as mentioned also by Braun and Manz (*Annalen*, 1929, **468**, 274) presents unusual difficulties and the present authors did not succeed in getting the acid by the direct hydrolysis of the nitrile either with alcoholic potash or sulphuric acid, but obtained the corresponding amide on hydrolysis with alcoholic potash while with sulphuric acid the reaction proceeded one step further and large quantities of fluorenone were obtained. The amide obtained with alcoholic potash on further hydrolysis with 20% hydrochloric acid was almost quantitatively converted into the corresponding acid

Pictet and Gonset (*Chem. Zentrl.*, 1897, I, 413) and Fanto (*ibid.*, 1899, I, 424) claimed to have prepared *o*-phenylbenzaldehyde by the pyrolysis of a mixture of the calcium salts of *o*-phenylbenzoic acid and formic acid. The details are, however, meagre and incomplete.

Having prepared the corresponding nitrile by an easy method (*J. Indian Chem. Soc.*, 1944, **21**, 27) the present authors attempted to prepare the aldehyde by Stephen's method (*J. Chem. Soc.*, 1925, 1874). Repeated attempts in this direction have failed to give the aldehyde inspite of different modifications including those mentioned by King and Robinson (*J. Chem. Soc.*, 1933, 273) and King, Liguori and Robinson (*ibid.*, 1933, 1476). King, L'Ecuyer and Openshaw (*ibid.*, 1936, 352) have also recorded similar experiences in preparing the corresponding aldehydes from α-napthonitrile and *o*-tolunitrile.

The authors next adopted a method described by Houben and Doscher (*Ber.*, 1907, **40**, 4576). An ethereal solution of *N*-methylformanilide has been made to react with the magnesium derivative of *o*-iododiphenyl. The resulting compound is hydrolysed by means of dilute hydrochloric acid. On extraction with ether and fractional distillation in vacuum *o*-phenylbenzaldehyde has been obtained in fairly good yield.

$$\mathrm{Ph{\cdot}C_6H_4{\cdot}MgI + Ph{\cdot}N(Me)CHO \longrightarrow Ph{\cdot}N(Me)HC}\begin{cases}\mathrm{OMgI}\\ \mathrm{C_6H_4{\cdot}Ph}\end{cases} \xrightarrow{H_2O}$$

$$\mathrm{Ph{\cdot}N(Me)H + Ph{\cdot}C_6H_4{\cdot}CHO}$$

Phenylcinnamic acid has also been obtained in good yield by the condensation of the aldehyde with malonic acid (*cf.* Pandya and Vahidy, *Proc. Ind. Acad. Sci.*, 1936, **4A**, 154).

The authors are at present engaged in preparing derivatives of this cinnamic acid with a view to utilising it as the starting material for a new synthesis of phenanthrene and its derivatives.

Experimental

o-Phenylbenzamide.—*o*-Cyanodiphenyl (2 g.) was gradually added to alcoholic potash (20%, 25 c.c.) and the mixture heated on the water-bath for 3 hours. The alcohol was recovered and water was added to the residue when a crystalline product was obtained, which was filtered, washed with water and crystallised from hot water as colourless needles, m.p. 177°, yield 1·8g.

(82%). (Found: C, 79·20; H 5·54; N; 7·04. Calc. for $C_{13}H_{11}ON$: C,79·17; H, 5·58; N, 7·10 per cent).

o-Phenylbenzoic Acid.—*o*-Phenylbenzamide (1 g.) was heated for 2 hours with hydrochloric acid (20 c. c., 1:1). A green oily liquid was produced, which solidified on cooling. The supernatant hydrochloric acid was decanted and the solid dissolved in sodium carbonate solution. The solution was acidified and the precipitate crystallised from 40% alcohol, m.p. 113·5°, yield 0·76 g. (76%). (Found: C, 78·83; H, 4·94. Calc. for $C_{13}H_{10}O_2$: C, 78·78; H, 5·5 per cent).

o-Phenylbenzaldehyde.—*o*-Iododiphenyl (1 mol., 28 g.), dissolved in absolute ether (100 c.c.), was treated with magnesium turnings (2·5 g.) in an atmosphere of nitrogen, stirred with a mechanical stirrer and freshly distilled methyl formanilide (13·5g.), prepared from monomethyl aniline and formic acid dissolved in absolute ether (35 c.c.), was added in the course of 2 hours. A vigorous reaction set in and a copious white precipitate was obtained. Any ether evaporating off was made up by the addition of ether from time to time. The stirring was continued for 1 hour in an inert atmosphere of nitrogen. The magnesium compound produced was decomposed by adding large quantities of crushed ice and hydrolysed by acidification with dilute hydrochloric acid. The ethereal layer was separated and the aqueous portion further extracted with ether. The combined ethereal extracts were dried over calcium chloride, the ether distilled off and the residue distilled at 150°/7 mm. as a light coloured oil, which darkens on keeping for a few days, yield 12·2 g. (67%).

o-Phenylbenzaldehyde-phenylhydrazone, prepared as usual, crystallised from alcohol as golden yellow crystals, m.p. 139.°. (Found: C, 83·84; H, 5·82; N, 10·24. $C_{19}H_{16}N_2$ requires C, 83·81 ; H, 5·88 ; N, 10·30 per cent). It gives a crystalline bisulphite compound with sodium bisulphite.

o-Phenylcinnamic Acid.—A mixture of *o*-phenylbenzaldehyde (3·6 g.) and malonic acid (3 g.) containing five drops of dry pyridine were heated on a water-bath for 4 hours. During the last hour the reflux condenser was replaced by an air condenser to allow the resulting water to be expelled. On cooling a precipitate was obtained, which was collected and washed with ice-cold water containing a few drops of dilute sulphuric acid. It was dissolved in sodium carbonate solution and reprecipitated with dilute sulphuric acid. It crystallised from alcohol as colourless light crystals, m.p. 202°, yield 3·22 g. (72%). The acid is soluble in ether, alcohol and chloroform. (Found: C, 80·41; H, 5·31. $C_{15}H_{12}O_2$ requires C, 80·37 H, 5·34 per cent).

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THE CONDENSATION OF ALDEHYDES WITH AMIDES. PART XI. THE CONDENSATION OF *m*-TOLYLALDEHYDE

By Premnarain Agarwal, Kantilal C. Pandya and Indralal Tripathi

m-Tolylaldehyde has been condensed with various amides in the presence or absence of an organic base. yielding in each case the corresponding *m*-tolylidene-bisamides.

Following the condensations of *p*-tolylaldehyde with amides (Part III, Mehra and Pandya, *Proc. Ind. Acad. Sci.*, 1939, **9A**, 508), the present paper describes the condensation of *m*-tolylaldehyde with the usual amides in the presence or absence of an organic base like pyridine. The products in all the cases have been shown to be the corresponding *m*-tolylidene-bisamides. The yields are not very high, being below 50%, though on the whole *m*-tolylaldehyde gives slightly higher yields than *p*-tolylaldehyde. Longer heating does not improve the yields and the presence of pyridine accelerates the condensation and slightly increases, in some cases, the yield.

Experimental

Condensation with Formamide.—Heating the aldehyde and the amide with a trace of pyridine (1: 2: 0·15 mol.) on a water-bath for 5 hours did not bring about the condensation. Heating at 115° for 8 hours in an open flask resulted in the formation of about 15% of the product. Heating in an oil-bath at 140° for 8 hours increased the yield to 29%, while the maximum of about 48% yield was obtained on heating at 160-170° for 8 hours. Heated also without pyridine, but in the same way in other respects the yield was almost the same, 47·6%. It was also found that heating in a flask provided with a reflux condenser gave no solid, and the aldehyde was recovered unchanged.

The reaction product was first extracted with water to remove the unchanged amide and then crushed with ether in a mortar to remove the remaining aldehyde and then filtered and recrystallised.

The crude product melted at 132-36°. Crystallisation from hot alcohol raised the melting-point ultimately to 139-40°. (Found :N, 14·72. $C_{10}H_{12}O_2N_2$ requires N, 14·59 per cent). The *bis*formamide came out in fine silky needles. It is insoluble in water, ether and benzene ; very sparingly soluble in methyl alcohol ; more soluble in hot ethyl alcohol or hot acetone. It does not decolourise Baeyer's reagent in alcoholic solution or bromine water. On refluxing with dilute sulphuric acid it breaks down into the aldehyde and the amide. It gives no colour with concentrated sulphuric acid.

With Acetamide.—The aldehyde was heated with acetamide in the same way as above but the temperature of the oil-bath was kept at 115-125° and the heating was continued for 5 hours. The crude product melted at 216° while the pure product melted at 224°. The yields in the absence of pyridine were 40·9% (crude) and 38·6% (pure), in the presence of a trace of pyridine, 50% (crude) and 43·2% respectively. (Found: N 12·92, 13·04. $C_{12}H_{16}O_2N_2$ requires N, 12·73 per cent). Its properties are similar to those of the bisformamide. It is insoluble in water, ether, benzene, acetone and chloroform, sparingly soluble in ethyl acetate and more in hot alcohol.

With Propionamide.—Heating for 5 hours at 115-125° gave 36·3% yield in the presence of a trace of pyridine, and 35·9% in the absence of pyridine. After 2 hours' heating evolution of water vapour and a gradual solidification of the reacting mass were observed, as before.

After the heating, the product was taken out next morning in the usual way. The crude product was fairly pure, as it melted at 194-97°, while the recrystallised (from hot acetone) product melted finally at 200-201°. It came out in white silky flakes, being insoluble in water, ether and ethyl acetate, slightly soluble in cold and more soluble in hot alcohol or acetone. (Found : N, 10·98. $C_{14}H_{20}O_2N_2$ requires N, 11·29 per cent). Its properties are similar to those of the other products described above.

With n-*Butyramide*.—Heated in the same way as above, the mixture went into solution in 1 hour and the usual observations were made. The yield, with pyridine, was 39·8%, and in its absence was rather less, 34·4%. The crude bisamide melted at 160-67°, and after two recrystallisations from hot alcohol the final m.p. was 170-71°, 10 hours' heating made no increase in the final yield. (Found : N, 10·36. $C_{16}H_{24}O_2N_2$ requires N, 10·04 per cent.

With n *Heptamide*.—The condensation was much slower and the heating was for 10 hours between 115-25°, 18 hours' heating in another experiment did not increase the yield, which was 35% in the presence of pyridine, and 38·2% in its absence. The crude bisamide melts at 112-16° ; recrystallised from hot acetone twice, the m.p. rises to 118°. It is obtained as silky needles, insoluble in water and ether; sparingly soluble in methyl alcohol, soluble in hot acetone or hot ethyl alcohol, very soluble in ethyl acetate. (Found: N, 7·57, 7·63. $C_{22}H_{36}O_2N_2$ requires N, 7·77 per cent).

With Benzamide.—The heating was for 5 hours, but two experiments were made in the presence of pyridine ; in the first only 0·15 mol. of pyridine was taken, and in the second, as a white sublimate was seen on the upper portions of the flask, it was continually washed down into the flask with a few more drops of pyridine, in this way a whole molecule of pyridine was used. The yield, however, was identical in both the cases, namely 37·7%, while in the absence of pyridine it was distinctly less, 31·9%. The crude bisamide melted at 186° or slightly above ; recrystallised from hot acetone, the m.p. rises finally to 221°. (Found: N, 8·53. $C_{22}H_{20}O_2N_2$ requires N, 8·13 per cent). Its solubility and other properties are similar to those described above.

With Phenylacetamide.—Phenylacetamide was prepared as before (Pandya and Sodhi, *Proc. Ind. Acad. Sci.*, 1938, **7A**, 367) and was heated with the aldehyde as above, with and without pyridine, for 5 hours between 120° and 130°. The crude yield was very good, m.p. at 184°. On recrystallising from hot alcohol once and from hot acetone afterwards, the final melting point was 199°. The yields were 48·38% in the presence of pyridine and 47% in its absence. (Found: N, 7·17. $C_{24}H_{24}O_2N_2$ requires N, 7·53 per cent).

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PARACHOR OF MOLECULAR IODINE AND OF POTASSIUM IODIDE IN WATER

By W. V. Bhagwat and S. O. Shukla

The parachor of molecular iodine is about 192 as determined in ethyl alcohol and benzene. The value is more than double for atomic iodine (91). The variation is similar to that in the case of Br_2, Cl_2, H_2, etc. Parachor of KI in water varies from 150-156 for molar fractions of KI ranging from 0·0325 to 0·0989.

The parachor of atomic iodine is determined by Sudgen (Sugden, "Parachor and Valency", p. 180) by the study of organic compounds of the elements. The value is 91·0. However, the value in solution is not known. This must correspond to the parachor of molecular iodine. The values in ethyl alcohol and benzene are given below. x stands for the molar fraction of iodine and $1-x$ for molar fraction of the solvent.

TABLE I

x.	$1-x$.	M_m.	Temp.	D.	γ.	P_m.	P_x.
Parachor of molecular iodine (I_2) is ethyl alcohol.							
0·0185	0·9815	50 01	25°	0·8539	22·8	127·9	193·7
0·0328	0·9672	52·85	25°	0·9024	23·45	128·8	190·9
0·0408	0·9591	54·51	25°	0·9320	23·68	129·0	189·9
Parachor of I_2 in benzene (parachor of benzene = 206·5).							
0·0182	0·9818	80·75	25°	0·9170	30·14	206·14	196·2

The results indicate that the value of molecular iodine, I_2, is near about 192. This is more than twice the value for atomic parachor of iodine (91). Iodine molecule has covalent link and Sudgen assumes that single covalent link does not contribute towards parachor and the value for molecular iodine I-I should be $2 \times 91 = 182$. However, the result is not surprising since this deviation between the values of atomic and molecular parachor seems to be common, as will be illustrated by the following results in Table II (*vide* Sugden, "Parachor and Valency", p. 187).

TABLE II

Atomic parachor	Molecular parachor Obs.	Molecular parachor Calc. from atomic parachor
Br = 68	Br—Br = 132·1	136
Cl = 54·3	Cl—Cl = 111·5; 104·6	108·6
H = 17·1	H—H = 35·2	34·2
N = 12·5	N=N = 60·4	25
O = 20	O=O = 54·2	40

A double bond contributes by 23·2 and a triple bond by 46·6 towards parachor. Hence parachor of N_2 should be 71·6 and of O_2, 63·2. It is clear therefore that there are other factors which govern the parachor in molecular state than the simple relation. The value of 192 for I_2 is therefore not at all surprising.

Jager (*Z. anorg. Chem.*, 1917, **101**, 1) has determined the surface tension of fused potassium iodide at several temperatures between 737° and 812°. These values have been utilised by

Sudgen (*loc. cit.*, p. 178) to determine its parachor. The values range between 204·3 and 206·9 and the value 205·2 is taken as a mean. From the values of parachors of fused potassium salts the value of atomic parachors of potassium comes out to be 110. Actually the value fluctuated from 84 to 115. Similar work with sodium salts give $P_{Na}=80$. Actual determination of parachor of sodium by fusing it, gives a value 97·4 (Pointdexter, *Physical Rev.*, 1926, **27**, *ii*, 820). This suggests that value of P_K as obtained by Sudgen may not be reliable.

Ray's work (*J. Indian Chem. Soc.*, 1938, **15**, 46) on potassium iodide in aqueous solution gives a value 103·1—145·2 for molar fraction of KI=0·11 to 0·086. These values are very different from that of fused salt. Ray's results are for one definite temperature and the values of surface tension are neither gradually increasing or decreasing. Inspite of this the value of parachor steadily increases with the increase of molar fraction. The results need revision. Our results are as follows.

TABLE III

Parachor of potassium iodide in water (Parachor of $H_2O=52·44$)

x.	$1-x$.	M_m.	Temp.	D.	γ.	P_m.	P_x.
0·0325	0·9675	22·85	25°	1·2044	74·66	55·63	150·8
,,	,,	,,	30°	1·201	72·26	55·67	152·0
0·0491	0·9509	25·27	25°	1·296	75·51	57·45	154·64
0·0789	0·9211	29·69	25°	1·454	77·14	60·5	154·6
,,	,,	,,	30°	1·449	75·2	60·29	151·95
,,	,,	,,	40°	1·442	72·92	60·16	150·3
0·6989	0·9011	32·64	25°	1·552	79·29	62·74	156·6
,,	,,	,,	30°	1·546	77·41	62·64	155·5
,,	,,	,,	40°	1·539	75·37	62·5	154·1
,,	,,	,,	50°	1·530	72·85	62·34	152·5

The deviation observed in case of Ray's results may be due to the fact that the molar range investigated by him is large while the mixture law gives consistent results provided molar fractions of the solute and solvent do not differ widely.

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STUDIES ON THE COMPOSITION OF PEPTONES. PART III

By Sudhindra Nath Sen

Absorption of formaldehyde by different brands of peptones has been studied. From the absorbtion curves similarity in composition can be inferred among some of them.

It is known that a protein molecule reacts with formaldehyde and the linkage takes place mainly at groups other than the peptide chain (-CONH-). The formaldehyde might react with one or other reacting groups that may remain free in any particular protein or its hydrolysed products. As such a study on the mode of such reactions and absorption might offer a clue to the nature of the union of the various amino-acids that build up a protein molecule and thereby a differentiation may be made between proteins of apparently same nature. In this paper certain observations on the behaviour of formaldehyde with certain animal proteins and some varieties of commercial peptones have been made.

Experimental

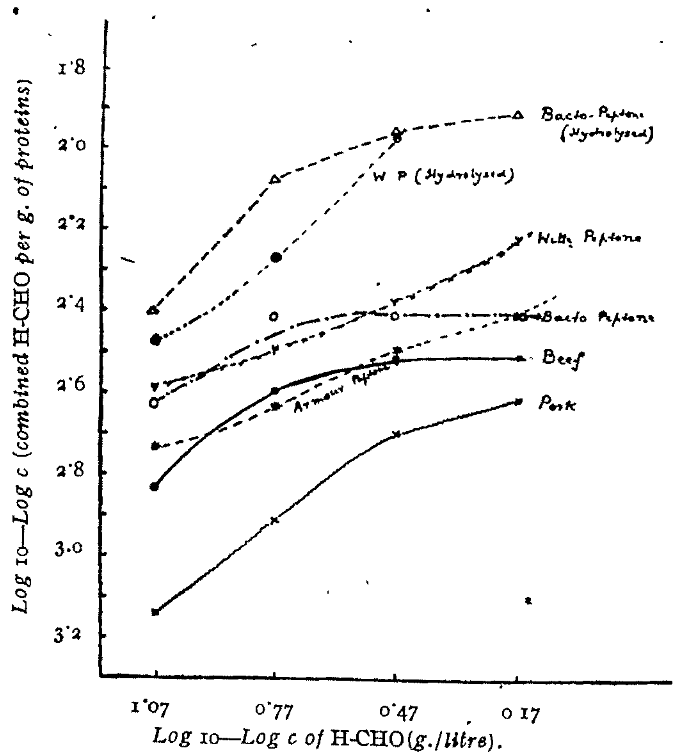
Different proteins as well as well as different varieties of commercial peptones were taken for experiment. In the case of protein 5 g. of the sample (fat-free and well minced) were taken in a stoppered phial, 50 c.c. dipotassium hydrogen phosphate solution (0·05 *M*) were added. Formaldehyde solution (8·5%), previously neutralised to p_H 7·0, was added in volumes of 1 c.c., 2 c.c. 3 c.c. and 4 c.c. and the final volume was made up to 100 c.c. with K_2HPO_4 (0·05 *M*) solution. Amount of moisture present in the sample was taken into account when diluting the volume to 100 c.c. In the case of peptone 1 g. was dissolved in K_2HPO_4 solution (0·05 *M*), formaldehyde was added in different concentrations and the final volume was made up to 100 c.c. with K_2HPO_4 solution.

In each case a few c.c. of toluene were added and the whole was incubated at 30° for 24 hours. Moisture was determined by keeping the substance at 105° till the weight became constant. After 24 hours, free formaldehyde was estimated by dimedone reagent according to the method of Wordsworth and Pangborn (*J. Biol. Chem.*, 1936, I, 116). The dimedone-formaldehyde compound was always purified by acetone, filtered in a gooch crucible, dried at 110-120° for 2 hours and weighed. Formaldehyde was calculated by using the factor 0·1027 per mg. of the compound and by difference formaldehyde absorbed was determined. Moreover, Witte peptone and Bacto-peptone were separately hydrolysed with hydrochloric acid (6 *N*), the acid was practically removed in vacuum and then neutralised. An 1% solution was made with K_2HPO_4 solution (0·05 *M*) and treated with different concentration of formaldehyde as usual. The weight of formaldehyde (in g.) absorbed per g. of the different nitrogenous materials in 24 hours at 30° is shown in Table I; the graph indicates the logarithm of the formaldehyde concentration per litre against that of the formaldehyde adsorbed per g. of the protein or the peptone material.

Table I

	g. of HCHO absorbed per g. of substance			
Conc. HCHO (g./litre).	0·85	1·7	3·4	6·8
(1) Witte peptone	0·0258	0·0325	0·0426	0.0604
(2) ,, (hydrolysed)	0·0342	0·0531	0·1070	—
(3) Bacto-peptone	0·0234	0·0385	0·0385	0·0385
(4) ,, (hydrolysed)	0·0394	0·0850	0·1100	0·1227
(5) Armour peptone	0·0190	0·0232	0·0326	0·0392
(6) Beef	0·0149	0·0259	0·0306	0·0309
(7) Pork	0·0073	0·0124	0·0200	0·0241

From the experiment so far carried out with the absorption of formaldehyde with different proteins and peptones it appears that some of them are similar in nature (*vide* graph). . Since the absorption of formaldehyde by protein or its breakdown products such as peptones depends on the arrangement of different polar groups in the molecule, it may be taken that absorption curves of proteins with similar group arrangement in the molecule will run parallel and those for protein of different arrangement will cut each other (*cf.* Bacto-peptone and Witte peptone, both hydrolysed and non-hydrolysed). In the breakdown products of proteins, the results are as might be expected. The process of hydrolysis by acids or enzymes opens up new groups by fission, there is a greater absorption of formaldehyde and the absorption curves run parallel; only the degree of absorption varies (*cf.* Witte peptone and Bacto-peptone). From the curves, the existence of a similar group arrangement may be inferred in beef and bacto-peptone, whereas a similarity exists amongst Witte peptone and Armour peptone.



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UTILIZATION OF GROUNDNUT MEAL

By U. P. Basu and S. K. Sen-Gupta

Groundnut meal has been assayed; the nitrogenous matter as present in the nuts has been extracted by different processes and the proteinous body of the meal has been subjected to the digestive action of various enzymes.

It was previosuly observed (Basu and Ganguly, *Proc. Ind. Sci. Cong.* 1944, Part III, p. 48) that a flour rich in protein, mineral and vitamin contents and suitable for human consumption may be prepared from groundnut meal. Groundnnt oil has been removed from ground nut by mechanical press and the meal left behind is used either as a fodder or a fertilizer. Certain characteristics of this meal are now being compared with one that has been obtained in this laboratory by drying the decorticated groundnuts, removing the pericarp and finally extracting out the oil from the powdered groundnut meal by means of petroleum ether (b. p. 50-60°). It may be mentioned here that as groundnuts are being largely produced in India, any knowledge that may be gathered on the development of a method of extracting the oil and thereby, getting a better type of meal, would go a long way for the improvement of ground nut oil industry in the country. The residual meal may be properly utilized not only as food, but also in the production of adhesives, plastics, water-paints and allied materials.

Experimental

The hydraulic-pressed cake, as kindly supplied by Messrs. Swaika Oil Mills, Calcutta, was used in this investigation. This was finely powdered in a mill (60 mesh), and was then stored at room temperature (30°) in large glass-stoppered bottles previously cleaned and dried at 150°. This and the solvent-extracted meal were analysed and the results are being recorded in Table I.

Table I

Comparative analysis of pressed meal and solvent-extracted meal.

Substance	Moisture	Ash	Ether extract	Protein	Fibre	Carbohydrate	Nicotinic acid (mg / 100 g.).
Pressed meal	8·1%	5·75%	5·43%	52 93%	5·71%	22 08%	28
Solvent-extracted meal	6·05	5·1	8·82	49	6·2	24 83	25

Each of the above meals was assayed for its nitrogen content and then extracted under different conditions. It may be recorded here that 90 to 95% of the nitrogen in groundnut meal is present as protein nitrogen (*cf.* Higgins *et al*, *Agr. Expt. Sta. Bull.*, 1941, No, 213, p. 3). The amount of nitrogenous substances extracted by the process, described below, was determined by finding out the nitrogen per cent in the extract by the macro-Kjeldahl method on aliquots of the clear centrifugates. The total amount of nitrogen in the solvent added was then calculated out. From this the percentages of total nitrogen extracted out from the cake in question were found out and are recorded in Tables II and III. Usually 2·5 g. of the powdered meal were taken for extraction with about 100 c.c. of different solvents, and were kept for one hour at the room temperature with occasional shaking. After the period, the whole was centrifuged and an aliquot part of the supernatant liquid was taken for estimation.

The solvent-extracted meal was then subjected to enzymatic digestion by papain (Ceylon variety) at p_H 5·5 (A); papain after activation with sulphuretted hydrogen according to the method of Frankel *et al.* (*Biochem. J.*, 1937, **31**, 1926) (B); by trypsin at p_H 8·1 (C); by trypsin in presence of 15% alcohol (D); by pepsin (B. D. H.) at p_H 1·8 (F), and directly by hydrochloric acid (20 per cent) under reflux for 18 hours (E), to see what percentages of nitrogenous matter as present in the meal, might undergo a peptization under varying condi-

tions. For this, 10 g. of the meal were at first suspended in 100 c.c. of water in presence of the respective enzymes at 50°. In case of papain 2·5 g. of the enzyme were used for each experiment (20 c.c.); whereas in case of pepsin only 1 g. of the enzyme was used. From the suspension 10 c.c. of the supernatant liquid were taken, treated with 5 c.c. of trichloroacetic acid (5%) to free it from any protein and the filtrate was assayed for finding out the soluble nitrogen by the usual Kjeldahl method. Similar experiments were carried out in presence of each enzyme after digesting the mass for a period of 24 and 96 hours. From these, the amount of the meal that has undergone peptization was found out as above, after trichloroacetic acid treatment, and the respective data under varying conditions as obtained from an average of three experiments are recorded in Table IV.

TABLE II

Pressed meal containing 8·47% N.

Expt.	Extraction solvent	p_H of suspension	% of total meal N extracted
1	NaOH (4%)	10	85 3
2	,,	8 5	69·5
3	NaOH and NaCl (6%)	,,	55
4	,,	7·5	56
5	Dilute NH_3 (1:1)	8·5	65·2
6	Dilute NH_3 and NaCl (6%).	8·5	65

TABLE III

Solvent-extracted meal containing 7·84% N.

Expt.	Extraction solvent	p_H of suspension	% ot total meal N extracted
1	NaOH (4%)	10	88·3
2	,,	8·5	75·2
3	NaOH and NaCl (6%)	,,	77
4	,, ,,	7·5	60
5	DiluteNH$_3$ (1:1)	8 5	72
6	,,	7·5	70·5
7	DiluteNH$_3$ and NaCl (6%)	8·5	74·8

TABLE IV

Solvent-extracted meal containing 7·84% N.

Expts.	Total meal N undergoing peptization: 0 hour	24 hours	96 hours
'A'	20%	54%	56%
'B'	22	60	64
'C'	25	60·5	70
'D'	20	71·3	82·5
'E'	20	62·8	74·5
'F'	...	100*	...

* in 18 hours

From Table I, it may be noticed that chemically the pressed meal does not appreciably vary from the solvent-extracted one. But while extracting out the nitrogenous matter from the respective meals it has always been noticed (*vide* Tables II and III) that solvent-extracted meal always gave a larger yield of nitrogenous matter in the extract. This shows that most probably under the high pressure of the hydraulic press which is usually used in extracting the oil from groundnut, the nitrogenons body as present in groundnut has undergone some changes that lower down its solubility in the various solvents that have been employed throughout the course of this investigation. This characteristic change in the protein molecule of groundnut in the pressed cake is also being noticed in connection with other experiments which are also in progress in this laboratory. It is always being noticed by us that the nitrogenous constituents are better extracted at p_H higher than 8·5. Fontaine and Burnett (*Ind. Eng. Chem.*, 1944, **36**, 164) have noticed that more than 90 per cent of the nitrogenous constituents can be peptized at p_H 7·2 or above if the meal be allowed to stand for 3 hours at room temperature (25°). From the data in Table IV it would be evident that the proteinous nitrogen as present in the meal (solvent-extracted) has undergone a proteolytic cleavage under the influence of all the common proteolytic enzymes. In this respect trypsin in presence of alcohol (Experiment D) is most effective. More than 82% of the nitrogenous body as was present in the meal could be recovered by the latter process.

Further work on the characteristics of the protein as present in the groundnut as well as on the nature of their fragmented molecules after enzymatic digestions is in progress. It is also being contemplated to find out the difference, if any, in the charactertistics of the proteinous body that might be extracted out from the groundnut by the different solvents.

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STUDIES IN INDIGOID DYES. PART IV

By Sisir Kumar Guha

The 7-methyl derivatives of *bis*-2-thionapthene-ethylene-indigo and of 2-thionaphthene-1′-aceanthrylene-indigo have been prepared. Their dyeing shades on wool and on cotton have been found lighter than those obtained from the corresponding 4-, 5- and 6-methyl compounds.

7-Methyl derivative of benzylidene-2-thianaphthene and some of its substituted products have been prepared. Their dyeing shades have been found lighter than those obtained from the corresponding substances of the 4-, and 5-methyl series but deeper than those obtained from the corresponding 6-methyl compounds.

From the examination of colour and dyeing properties of a large number of isomeric indole-(methyl)-thionaphthene-indigos and all the isomeric dimethyl-thioindigos, it was deduced that their depth of colour decreases as the methyl group is shifted from 5 to 4 to 6 to 7-position of the thionaphthene nucleus of the molecule of the dye and also observed that the depth of colour of the parent compound of each series is next to that of its 5-methyl derivative (Guha, *J. Indian Chem. Soc.*, 1944, **21**, 87).

With a view to testing further how far this observation is applicable to other thioindigoid dyes of asymmetrical as well as symmetrical structure, 2-thionaphthene-1′-aceanthrylene-indigo and *bis*-2-thionaphthene-ethylene-indigo (D.P. 250157, 253762; Friedlander and Risse, *Ber.*, 1914, **47**, 1919) were selected as respective examples.

The influence of a methyl group in 4-, 5-, and 6-position of the thionaphthene nucleus of the parent dye in each of the two above mentioned series was already studied in previous parts of this series (Guha, *J. Indian Chem. Soc.*, 1935, **12**, 658; 1937, **14**, 709; 1938, **15**, 359). In the present communication the effect of a methyl group in the 7-position of the thionaphthene ring of *bis*-2-thionaphthene-ethylene-indigo and 2-thionaphthene-1′-aceanthrylene-indigo has been studied.

7-Methyl-3-hydroxy-thionaphthene (Guha, *J. Indian Chem. Soc.*, 1943, **20**, 37) has been condensed with glyoxal and aceanthrenequinone respectively. The two new vat dyes are crystalline deep red and dark red substances. Their dyeing shades on wool and on cotton have been found lighter than those obtained from the isomeric 4-, 5- and 6-methyl derivatives. In both the series this qualitative inference has been verified by measuring the absorption spectra of the dyes in xylene solution and calculating the absorption maxima (Table I) from their absorption curves (Figs. 1, 2 and 3).

It is, therefore, summarised from the detailed study of all the theoretically possible isomeric *bis*-(methyl)-thionaphthene-ethylene-indigos and (methyl)-thionapthene-aceanthrylene-indigos (Table I) that the 5-methyl products are the deepest of all, second is the position of the 4-methyl compounds, the 6-methyl products occupy the third position and the lightest are the 7-methyl-indigos. The parent dye *bis*-2-thionaphthene-ethylene-indigo is lighter only than its 5-methyl derivative.

It is thus found that the relation between colour and chemical constitution of all the isomeric *bis*-(methyl)-thionaphthene-ethylene-indigos and (methyl) thionaphthene-aceanthrylene-indigos deduced now is in good agreement with what was was already found by the author in case of quite a number of isomeric indole-(methyl)-thionaphthene-indigos and all the isomeric dimethyl-thioindigos (Guha, *loc. cit.*).

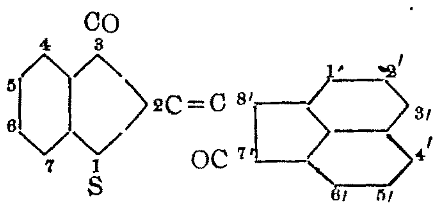
The different shades of the isomeric *bis*-(methyl) thionaphthene-ethylene-indigos on wool and on cotton are beautiful but that of the 6-methyl compound is particularly pleasing and attracting.

In Tables I, II and III, M = Methyl, T = Thionaphthene, B = Benzylidene.

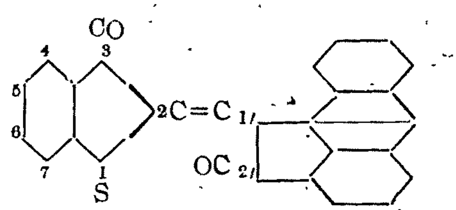
TABLE I

Compounds.	Absorption maxima.	Compounds.	Absorption maxima.
bis-2-T-ethylene-indigo	4835Å	2 (4-M)-T aceanthrylene indigo	4455Å
bis-2-(4 M)-T-ethylene-indigo	4810	2-(5-M)-T-aceanthrylene-indigo	4460
bis-2-(5-M)-T-ethylene-indigo	4920	2-(6 M)-T aceanthrylene-indigo	4450
bis 2 (6-M)-T-ethylene-indigo	4765	2 (7 M)-T-aceanthrylene-indigo	4410
bis-2-(7-M)-T-ethylene-indigo	4750		

When the studies in the isomeric (methyl)-thionaphthene-aceanthrylene-indigos were made complete, it struck that the corresponding compounds belonging to acenaphthenequinone series, the (methyl)-thionaphthene-acenaphthylene-indigos are much deeper in colour (Guha, *J. Indian Chem. Soc.*, 1944, **21**, 91). This led the author to conclude that as the complexity of the right half of the molecule of 2-thionaphthene-8′-acenaphthyleneindigo (I) is increased by fusing another six-membered ring into it, when for example 2-thionaphthene-1′-aceanthrylene indigo (II) is produced, the depth of colour of the new product is lightened which will be understood clearly from the instances cited under Table II.



(I)



(II)

TABLE II

Compounds.	Dyeing shade on wool.	Compounds.	Dyeing shade on wool.
2-T-8′-acenaphthylene-indigo	Scarlet	2-(6-M)-T-8′-acenaphthylene-indigo	Vermillion
2-T-1′-aceanthrylene-indigo	Orange brown	2-(6-M)-T-1′-aceanthrylene-indigo	Red brown
2-(4-M)-T-8′-acenaphthylene-indigo	Vermillion	2-(7-M)-T-8′-acenaphthylene-indigo	Dark red
2-(4-M)-T-1′-aceanthrylene-indigo	Dark-brown	2-(7-M)-T-8′-aceanthrylene-indigo	Red brown
2-(5-M)-T-8′-acenaphthylene-indigo	Scarlet red		
2-(5-M)-T-8′-aceanthrylene-indigo	Orange-brown		

A few thioindogenides have been prepared by condensing 7-methyl-3-hydroxy-thionaphthene with benzaldehyde, *p*-nitro-, and its *p*-dimethylamino derivative respectively. The aldehydes used in this 7-methyl series are the same as those used in the case of the corresponding 4-, 5-, and 6-methyl series described in parts I, II and III, for the convenience of a comparative study. The thioindogenides of the 7-methyl series are also coloured products which were obtained easily in crystalline form. They resemble the other isomeric methyl compounds in giving rise to characteristic colour by the action of concentrated sulphuric acid. The dyeing shades of all these substances on wool from an acid bath are fully and uniformly developed. But their shades do not appear fully on cotton from the alkaline hydrosulphite vat although they are uniform [*cf.* the isomeric benzylidene-(methyl) thionaphthenes. Guha, *loc. cit.*]

These shades are found lighter than those obtained from the corresponding 4- and 5-methyl compounds but deeper than those obtained from the corresponding 6-methyl products. The absorption curves (Fig. 4) and the absorption maxima (Table III) confirm the qualitative

FIG. 1

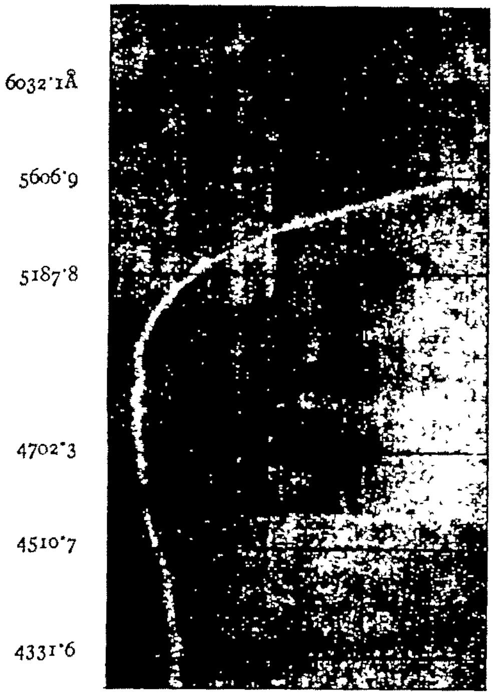


FIG. 2

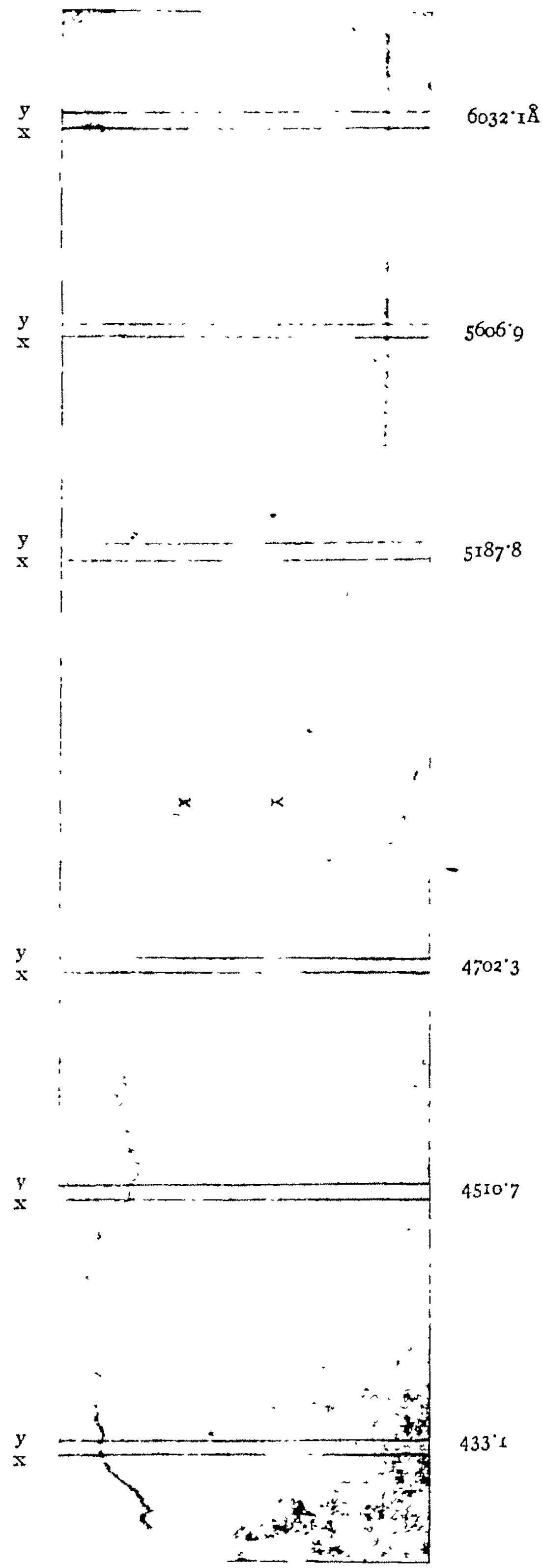


Fig. 1. Bis-2-(7-methyl)-thionaphthene-ethylene indigo.

2. x and y refer respectively to 2-(5-methyl)-, and 2-(4-methyl)-thionaphthene-1′-aceanthrylene indigo.

3. v and w refer respectively to 2-(7-methyl) and 2-(6-methyl) -thionaphthene-1′-ananthrylene indigo.

4. Benzylidene-2(7-methyl)-thionaphthene

FIG. 3

FIG. 4

observation. Hence the relation between colour and chemical constitution of the isomeric benzylidene-(methyl) thionaphthenes is found similar to that of the isomeric methyl thionaphthene-acenaphthylene-indigos (Guha, *loc. cit.*)

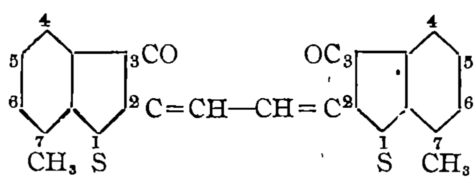
Of the various isomeric benzylidene-(methyl) thionaphthenes prepared, 4′-nitro-benzylidene-2-(5-methyl)-thionaphthene and all the isomeric 4′-dimethylamino-benzylidene-(methyl) thionaphthenes exhibit pleasant shade. It is found that none of the coloured products of the thioindogenide series, studied by the author, possess any value as vat dyes but all of them develop well on wool from an acid bath.

TABLE III

Compounds.	Absorption maxima.
B-2(4-M)-T	4400 Å
B-2(5-M)-T	4445
B-2(6-M)-T	4320
B-2(7-M)-T	4370

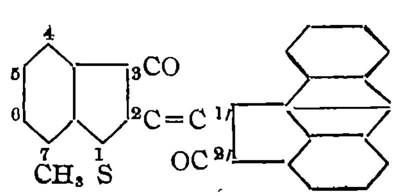
EXPERIMENTAL

bis-2-(7-*Methyl*) *thionaphthene-ethylene-indigo.*



A solution of glyoxal sodium bisulphite (1·136 g.) in distilled water (30 c.c.) was mixed with 7-methyl-3-hydroxy-thionaphthene (1·312 g.) dissolved in hot absolute alcohol (40 c.c.). The mixture on treatment with concentrated hydrochloric acid (20 c.c.) and heating on the water-bath for 1½ hours, gave a violet-red crystalline precipitate, which was filtered, washed with alcohol and hot water, yield 0·737 g. The dye was crystallised from xylene in deep red microscopic needles and also from pyridine in stout thin rectangles, not melting below 312°. It is difficultly soluble in toluene and chloroform; sparingly soluble in acetone, carbon tetrachloride, alcohol; moderately soluble in acetic acid. The solution of this dye in concentrated sulphuric acid is yellowish-green. It dyes cloth in violet-red shade from a deep yellow alkaline hydrosulphite vat and wool in dark-red shade from an acid bath. (Found: S, 18·27. $C_{20}H_{14}O_2S_2$ requires S, 18·28 per cent).

2-(7-*Methyl*)-*thionaphthene*-1′-*aceanthrylene-indigo.*



The hot solution of aceanthrenequinone (0·696 g.) and 7-methyl-3-hydroxy-thionaphthene (0·492 g.) in 80 c.c. of glacial acetic acid was treated with concentrated hydrochloric acid (sp. gr. 1·12, 5 c.c.). The mixture was boiled for 15 to 20 minutes in an atmosphere of carbon dioxide. The separated red product (0·75 g.) was collected while the solution was still hot. It is soluble in aniline and chloroform; difficultly soluble in pyridine, xylene and acetic acid; insoluble in alcohol. It was crystallised from a large volume of xylene in foliated shining dark red needles not melting below 304°. Concentrated sulphuric acid dissolves it with yellowish-green solution from which the original red substance is precipitated on the addition of water. It dyes wool in light red-brown shade from an acid bath and cotton in light red-ochre from a yellowish-green hydrosulphite vat. (Found: S, 8·11. $C_{25}H_{14}O_2S$ requires S, 8·46 per cent).

Benzylidene-2-(7-methyl)-thionaphthene.—It separated on boiling for 15 minutes benzaldehyde (0·424 g.) 7-methyl-3-hydroxy-thionaphthene (0·656 g.) in 13 c. c. of hot absolute alcohol, with concentrated hydrochloric acid (2 c.c.) The brownish-yellow product (0·741 g.) was crystallised from dilute alcohol in long rectangles, m.p. 130°. It is soluble in benzene, acetone and alcohol. Concentrated sulphuric acid dissolves it producing a deep brownish red solution. It dyes wool in yellow shade from an acid bath. (Found: S, 12·89. $C_{16}H_{12}OS$ requires S, 12·69 per cent).

4′-Nitro-benzylidene-2-(7-methyl)-thionaphthene was obtained as yellow-orange small rectangular precipitate by boiling for 15 minutes a solution of *p*-nitro-benzaldehyde (0·453 g.) and 7-methyl-3-hydroxy-thionaphthene (0·492 g.) dissolved in 26 c.c. of absolute alcohol and concentrated hydrochloric acid (3 c.c.) The coloured substance (0·7345 g.) was crystallised from acetic acid in rectangles, m.p. 247°. It is moderately soluble in alcohol, difficultly soluble in acetone. It dissolves in concentrated sulphuric acid producing a blue solution. It dyes cotton in light orange shade from a light brown alkaline hydrosulphite vat and wool in deep yellow shade from an acid bath. (Found: S, 11·0. $C_{16}H_{11}O_3NS$ requires S, 10·77 per cent).

4′-Dimethylamino-benzylidene-2-(7-methyl)-thionaphthene was obtained as its hydrochloride as a greenish-yellow crystalline precipitate by similarly boiling a red-brown solution of *p*-dimethylamino-benzladehyde (0·596 g.) and 7-methyl-3-hydroxy-thionaphthene (0·656 g.) in 17 c.c. of absolute alcohol and 2 c.c. of concentrated hydrochloric acid. It gave on washing with dilute alcohol the vermillion product (0·727 g.). It was crystallised from dilute acetic acid in wooly needles, m.p. 150°. It is soluble in alcohol and acetone. Concentrated sulphuric acid dissolves it with a blue-violet solution which on dilution with a little water turns yellow and when largely diluted gives the red precipitate of the original substance. It dyes cloth in pink colour from a faintly red alkaline hydrosulphite vat and wool in bright orange-red shade from an acid bath. (Found: S, 11·21. $C_{18}H_{17}ONS$ requires S, 10·84 per cent).

The author's thanks are due to Mr. K. Prasad I.E.S. and Dr. R. C. Ray D.Sc. for their interest in this work and to Messrs. D. K. Bhattacharya M.Sc. and K. S. Manian (Calcutta) for helping with spectrograph and microphotometer.

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A NOTE ON THE APPLICATION OF THE BOWMAN AND SCOTT METHOD FOR THE ESTIMATION OF NITROGEN IN GUNCOTTON

By B. N. Mitra and M. Srinivasan

The nitrogen content of guncotton is usually determined by the nitrometer. The reported errors of the method are due to (*i*) the solubility of NO in H_2SO_4 and (*ii*) the simultaneous formation of other gases from the degradation of the cellulose molecule (Beckett, *J. Chem. Soc.*, 1929, **117**, 220 ; Hill, *Analyst*, 1918, **48**, 215).

Other methods have been proposed alternative to the nitrometer method. Among these the one evolved by Bowman and Scott (*Ind. Eng. Chem.*, 1915, **7**, 766) for the estimation of small quantities of HNO_3 in oleum, has been adapted by Mange (*L. Ind. Chim.*, 1918, **5**, 255) for the estimation of nitrogen in guncotton ; the method does not, however, appear to have been used in the routine analysis of guncotton. According to Bowman and Scott the reaction is

$$4FeSO_4 + 2HNO_3 + 2H_2SO_4 \longrightarrow N_2O_3 + 2Fe_2(SO_4)_3 + 3H_2O$$

When HNO_3 has all reacted, N_2O_3 is reduced by excess of $FeSO_4$ to NO ; the end-point is the formation of the pinkish brown complex, $FeSO_4$—NO.

It was found that, following the details as given in Worden, ("Technology of Cellulose Esters," Vol. I, Part II, p. 978). reproducible results could not be obtained with guncotton. The following modifications were therefore found necessary.

(*i*) Ferrous ammonium sulphate (240 g. per litre in 60% H_2SO_4) was standardised against KNO_3, instead of against $K_2Cr_2O_7$; this obviated the correction in the titre suggested in the original method. (*ii*) Titration was effected at about 5°. (*iii*) In view of the high concentration of ferrous ammonium sulphate used (*vide infra*) titration was carried out in a burette reading to 0·05 ml.

The results obtained are detailed in Tables I and II.

Procedure

A known weight (about 0·5g.) of dried guncotton was introduced into a 250 ml. Erlenmeyer flask, 70 ml. conc. H_2SO_4 added and stoppered. The dissolution is effected with constant shaking at about 15°. After the guncotton has all dissolved, the flask is closed with a bored rubber-stopper and is placed in an ice-bath (a wide beaker is convenient). The standard titre is run in very slowly through a fine jet attached to the burette, the jet being well below the surface of the acid. The flask is shaken well throughout the tritration. Towards the end, the titration is effected dropwise, until a permanent pink colour is obtained. The estimation takes about half an hour. Following points should be carefully noted in this connection :

(*i*) The mixing of the titre with the contents of the flask must be thorough and intimate ; else, due to local concentration of ferrous sulphate, the $FeSO_4$—NO complex is precipitated, vitiating the result. Further, this pink-coloured precipitate obscures the end-point and cannot be redissolved unless by warming to room temperature. (*ii*) When within 1 ml. of the end-point, as determined in a preliminary run, the flask is to be taken out of the ice-jacket, and titration completed. While perfect cooling and very slow addition of titre are necessary in the early stages, to avoid (*a*) local heating leading to loss of HNO_3 and (*b*) formation of $FeSO_4$—NO complex with its disadvantages mentioned above, these precautions need not be strictly adhered to towards the end. (*iii*) For standardisation of ferrous ammonium

sulphate, about 0·5 g. of KNO_3 is a convenient quantity to work with. To obtain accurate results, about 0·5 g. of guncotton is taken for each test ; this weight contains nitrogen almost equivalent to that contained in the primary standard.

Besides estimating nitric acid, nitrates and guncotton, the method seems capable of estimating in general, all organic nitric esters, which yield nitric acid on dissolution in conc. H_2SO_4.

TABLE I

N content of a composite sample of guncotton as determined by

FeAm. Sulphate.	Nitrometer.
13·08	13·01
13·09	13·03
13·09	13·01
13·10	12·97
13·12	13·04
13·02	12·98
13·07	13·01
13·11	12·99
13·09	13·00
13·11	13·02
13·09	13·02
13·04	13·04

TABLE II

N content of different samples of guncotton as determined by

FeAm. Sulphate.	Nitrometer.
12·88, 0·87	12·97, 0·97
13·19, 0·22	13·02, 0·00
13·03, 0·02	13·01, 0·00
13·03, 0·00	12·98, 0·96
12·98, 0·99	12·88, 0·88
12·91, 0·93	12·90, 0·89
13·03, 0·05	13·06, 0·04
13·16, 0·14	13·01, 0·00
13·04, 0·08	13·02, 0·04
13·08, 0·10	13·07, 0·09
12·96, 0·95	12·95 —
13·20, 0·17	13·11, 0·09

The authors are indebted to Dr. H. R. Ambler, Ph.D., F.R.I.C., Chief Inspector of Military Explosives, for his kind interest in the work and to the Director of Armaments for kind permission to publish it.

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EVALUATION OF BARIUM PEROXIDE IN PRESENCE OF BARIUM SULPHIDE

By (Miss) Meher Timur and H. N. Das-Gupta

A method of estimating BaS and BaO_2 in a mixture of the two has been given. The process consists in the addition of $CdCl_2$ to the mixture when CdS and CdO_2 are formed. A part of this mixture is kept at 100° when CdO_2 is decomposed leaving CdS alone which is estimated. For estimation of peroxide it is treated with CH_3COOH and H_2O_2 liberated is estimated

In an attempt at preparing barium peroxide from barytes (Bradley and Jacob, B. P. 26060, 1898), a mixture, composing mostly of barium peroxide and the sulphide, was obtained. No analytical process is known for evaluating the peroxide content in a mixture like this. The well known permanganate method fails in this case owing to simultaneous generation of sulphuretted hydrogen and hydrogen peroxide. The present paper describes a process for estimating the percentage of barium peroxide in presence of the sulphide.

The process consists in treating the compounds with a solution of cadmium chloride which yields quantitatively a mixture of cadmium peroxide and the sulphide. The peroxide of cadmium is unstable at elevated temperatures and as such if a measure of the sulphide content alone is wanted the resulting mixture needs boiling for 10 to 15 minutes. This causes complete decomposition of the peroxide and the residual sulphide may then be estimated. For estimating the peroxide content or both, the solution needs treatment with dilute acetic acid, which yields an equivalent amount of hydrogen peroxide leaving the cadmium sulphide intact. The insoluble cadmium sulphide can easily be separated from the peroxide solution and each may be estimated separately. The process was standardised against artificial mixtures of Merck's pure barium sulphide and barium peroxide. The table following will show the results obtained by the adoption of the present method. Although different weights of the artificial mixtures of the two components were taken for analysis, in each case the calculation of the percentage of each component was made ignoring the proportion of the remaining component.

Experimental

Barium peroxide and barium sulphide were separately weighed and taken in a dry Erlenmeyer flask. This was then covered with previously cooled saturated solution of cadmium chloride (50 c.c. or more). The contents of the flask were well shaken and kept at a temperature not exceeding 5—8°. The resulting mixture was then acidified with dilute acetic acid in the cold and filtered quantitatively. For washing the precipitated cadmium sulphide, cold dilute acetic acid should be used. The filtrate was mixed with cold dilute sulphuric acid and titrated with standard potassium permanganate solution. The volume in c.c. of normal potassium permanganate required, multiplied by 0·084685 gives the weight of barium peroxide.

The residue left on the filter was transferred quantitatively in an evolution flask (capacity 200 c.c.), provided with a ground glass joint to which was attached a stoppered funnel (20 c.c. capacity). The stem of the funnel extended nearly to the bottom of the distilling flask ending in capillary. The side tube of the flask was connected to a system of four Erlenmeyer flasks, the first three containing standard iodine solution while the last one contained standard sodium thiosulphate solution. It was found necessary to maintain a constant flow of air through the entire system by means of a water-jet pump, connected to the exit end of the last wash bottle. This facilitated complete removal of the evolved sulphuretted hydrogen from the flask. For starting the experiment, pure concentrated hydrochloric acid should be

taken in the separating funnel and then the water-jet pump is to be started. The decomposition is promoted by warming slowly over a small flame. On cooling the contents of the wash bottles were mixed together and the excess of iodine titrated back with standard thiosulphate solution.

For estimating the percentage of barium sulphide alone the following procedure was adopted. The mixture was taken directly into the evolution flask and was treated with cadmium chloride solution. This gave immediately a precipitate of cadmium sulphide. The mixture was well shaken and then boiled for 10 to 15 minutes to decompose the unstable peroxide of cadmium. After this the sulphide was decomposed in the usual way and the liberated sulphuretted hydrogen absorbed in iodine.

It may be pointed out that the usual precautions for iodimetic method of estimating sulphides must be taken. The strength of iodine solution should preferably be maintained between $N/100$ and $N/10$. With more concentrated solution, the precipitated sulphur encloses a portion of the iodine, and this escapes subsequent titration with standard sodium thiosulphate solution. Results are given in the following tables :

TABLE I

Estimation af barium sulphide alone in a mixture af BaS *and* BaO_2

BaS (obs,) in %	...	91·507	91·510	91·510	91·506	91·505
BaS (calc.) in %	..	91·516	91·516	91·516	91 516	91·516

TABLE II

Estimation of barium peroxide and barium sulphide in a mixture

Substance.	Wt. taken.	% Calc.*	% Obs.
BaO_2	0·1439 g.	76·61	76·59
BaS	0·1300	91·516	91 52
BaO_2	0·1561	76·61	76 58
BaS	0·1124	91·516	91·53
BaO_2	0·2579	76·61	76·63
BaS	0·1237	91·516	91·60
BaO_2	0·3256	76·61	76 62
BaS	0·2147	91·516	91·52
BaO_2	0·3509	76·61	76·62
BaS	0·2091	91·516	91·60

* The figure was calculated on the assumption that the other ingredient was absent.

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ON THE ALKALOID ISOLATED FROM THE MATURED BARK OF *AEGLE MARMELOS*, CORREA

By K. K. Chakravarty

The alkaloid, isolated from the matured bark of *Aegle marmelos* (Bihar variety), has been proved to be identical with γ-fagarine, an alkaloid isolated by Stuckert and his collaborators from the leaves of *Fagara Coco*.

From the matured bark of *Aegle marmelos* (Bihar variety) Mookerjee (*Current Science*, 1943, **12**, 209) isolated three crystalline constituents, one of which is an alkaloid, m.p. 142°, the other two substances being neutral.

In the present communication is discussed the constitution of this alkaloid which has been named "aegelenin."

The alkaloid melts at 142° and is obtained in a yield of 0·3 per cent. It is fairly soluble in acetone, chloroform, sparingly in ether, ethyl acetate and alcohol and in petroleum ether and water. A solution of the base in alcohol is neutral to litmus and it is optically inactive. It does not contain any solvent of crystallisation. It does not produce any colouration with ferric chloride in alcohol but gives the following colour reactions:

TABLE I

	Reagent.		Colour.
1.	Conc. sulphuric acid	...	Colourless
2.	Conc. nitric acid	...	Yellow
3.	Frohde's reagent	...	Greenish yellow
4	Erdmann's reagent	...	Greenish yellow
5.	Mandelin's reagent	...	Pale red to deep red.

It dissolves freely in acids and gives an orange precipitate with Dragendorff's reagent and a chocolate brown precipitate with a solution of iodine in potassium iodide. It is a monoacid base, forms a deep yellow picrate and an orange chloroplatinate, both of which are crystalline.

The analyses of the base and its salts indicate the formula $C_{13}H_{11}O_3N$ which has been supported by the molecular weight data. The N-methyl determination (Herzig and Meyer, *Ber.*, 1894, **27**, 319; *Monatsh*, 1894, **15**, 613; *ibid.*, 1897, **18**, 382) and Gaebel's test for methylenedioxy group (*Arch. Pharm.*, 1910, **248**, 207) are negative but the presence of two methoxyl groups by the method of Zeisel-Pregl-Vieböck (*Ber.*, 1930, **63**, 2881, 3207; *Monatsh*, 1885, **6**, 989; 1886, **7**, 406) could be established. The base does not form any acetyl or benzoyl derivative thus suggesting the tertiary nature of the basic nitrogen atom.

TABLE II

Aegelenin m. p. 142°		*γ-Fagarine* m. p. 142°
Molecular formula	$C_{13}H_{11}O_3N$	Molecular formula $C_{13}H_{11}O_3N$
Picrate ($C_{13}H_{11}O_3N$ $C_6H_3O_7N_3$)	m. p. 176°	m. p 177°
Degradation products		
(a) Aldehyde ($C_{12}H_{11}O_4N$)	185° (decomp.)	185° (decomp.)
Phenylhydrazone of (a) ($C_{18}H_{17}O_3N_3$)	205° (decomp)	207° (decomp.)

Aegelenin		*γ-Fagarine*
Degradation products		
(b) Acid ($C_{12}H_{11}O_5N$)	m. p. 215° (decomp.)	m. p. 215° (decomp.)
(c) Decarboxylation product of (b) ($C_{10}H_9O_3N$)	248° (decomp.)	248° (decomp.)
(d) Nitroso derivative of (c)	216° (decomp.)	216° (decomp.)

These properties agree with those of γ-fagarine, isolated from the leaves of *Fagara coco* (Stuckert and his collaborators, *Investigationes del Laboratorio de Quimica Biologica Cordoba, Argentina*, Vol. I, 1933 and Vol. II, 1938; Denlofeu, Labriola and Laughe, *J. Amer. Chem. Soc.*, 1942, **64**, 2326).

As an authentic specimen of γ-fagarine could not be procured, the alkaloid was further degraded to the aldehyde and the acid and their properties compared with the corresponding products obtained from γ-fagarine.

The data presented in the Table II do not leave any doubt that the alkaloid of *Aegle marmelos* is identical with γ-fagarine.

EXPERIMENTAL

Isolation of γ-Fagarine.—Matured bark of *Aegle marmelos* (400 g.), collected from Bihar in the month of October, was dried in the sun, coarsely powdered and extracted with ether in a Soxhlet for 48 hours. The deep brown ethereal extract was digested with 0·1% hydrochloric acid (200 c.c. in instalments). The extraction was continued till the acid digest gave insignificant precipitate with Dragendorff's reagent. Four to five extractions were sufficient for the complete extraction of the base. The red acid aqueous solution was cooled in ice and basified with sodium bicarbonate. The base separating in flocks was taken up in ether (300 c.c.). The pale yellow ethereal extract was washed with water, dried over anhydrous sodium sulphate and distilled. The solid residue (1·2 g.), left on removal of ether, crystallised from ethyl acetate in colourless prisms, m.p. 142°. On repeated crystallisations from ethyl acetate, alcohol, and acetone, the m.p. could not be raised. There was no loss in weight when the crystals were dried in *vacuo* over P_2O_5 for 3 hours at 100°. (Found: C, 68·41; H, 4·85; N, 6·2; OMe, 27·22; Mol. wt. 227. Calc. for $C_{13}H_{11}O_3N$: C, 68·12; H, 4·8; N, 6·11; OMe 27·07 per cent. Mol. wt., 229).

Chloroplatinate.—To a cooled solution of the base (0·2 g.), dissolved in hydrochloric acid, platinic chloride solution (5%) was slowly added, till precipitation was complete. The orange flocculent precipitate was collected, washed with cold water containing a few drops of hydrochloric acid and crystallised from water acidulated with hydrochloric acid. The orange needles, thus obtained, decomposed on heating above 200° without melting. [Found in a dry sample: Pt, 22·52. $(C_{13}H_{11}O_3N)_2H_2PtCl_6$ requires Pt, 22·47 per cent].

The picrate of the base was prepared by adding picric acid solution to an alcoholic solution of the base. The crystals which separated on cooling were collected, washed with cold alcohol and crystallised from the same solvent. The yellow needles of the picrate melted at 175° (decomp.). On further crystallisation from other solvents there was no change in m.p. [Found in a sample dried in *vacuo* over P_2O_5 at 100° for 4 hours: N, 12·50. Calc. for $C_{13}H_{11}O_3N$, $C_6H_2(OH)(NO_2)_3$: N, 12·22 per cent].

Oxidation of the Base with Potassium Permanganate.—A solution of the base (0·5 g.) in acetone (30 c.c.) was gently boiled on a water-bath and a neutral solution of potassium permanganate (1·0 g. in 20 c.c. acetone) was added. The solution was then refluxed for ½ hour, cooled and filtered. The manganese dioxide residue (A) was thoroughly washed with boiling acetone. The pale yellow filtrate (B) was worked up as follows:

Isolation of γ-Fagaric Aldehyde.—The filtrate (B) was freed from the solvent and the residue was digested with an aqueous solution of sodium bicarbonate and filtered. The filtrate (C) was added to the manganese dioxide residue (*vide supra*) and the mixture was subsequently worked up for the acid (*vide infra*). The residue, insoluble in sodium bicarbonate, was

crystallised from acetone, alcohol and other solvents when shining yellow needles, m.p. 185° (0·25 g.) could be obtained. (Found in a dry specimen : C, 61·68 ; H, 4·91 ; N, 6 58 ; OMe, 26·85. Calc. for $C_{13}H_{11}O_4N$: C, 61·80 ; H, 4·72 ; N, 6·00 ; OMe, 26 61 per cent).

The *phenylhydrazone* crystallised from alcohol in yellow needles (0·2 g.), m.p. 205°, (decomp.). (Found in a sample dried in *vacuo* over P_2O_5 for 3 hours at 100° : N, 13·28. Calc. for $C_{18}H_{17}O_3N_3$: N, 13·0 per cent).

Isolation of γ-Fagaric Acid from the fraction (A) *and* (C).—The manganese dioxide residue and the sodium bicarbonate filtrate (C) (*vide supra*) were thoroughly digested with more sodium bicarbonate solution (aqueous) and filtered. The filtrate (50 c.c.) was cooled in ice, acidified with hydrocholoric acid (congo red), The flocculent precipitate was collected and crystallised from glacial acetic acid. The colourless crystals (0·1 g.) melted at 215° (decomp.). (Found in a dry specimen : C, 57·53 ; H, 4·61 ; N 5·80; OMe, 24·68. Calc. for $C_{12}H_{11}O_5N$: C, 57·83 ; H, 4·41 ; N, 5·62 ; OMe, 24·89 per cent).

Decarboxylation of the Acid.—The acid (0·25 g.) was suspended in dilute hydrochloric acid (40 c.c., *d.* 1·15) and boiled till a clear solution resulted. On concentrating the solution (5 c.c.) colourless crystals separated, m. p. 248° (decomp.). On crystallisatlon from alcohol, the substance had the same m.p. (Found in a dry sample: C, 62·95 ; H, 4·88; N, 7·50. Calc. for $C_{10}H_9O_3N$: C, 62·82 ; H, 4·72 ; N, 7·33 per cent).

Nitroso derivative of the Decarboxylation Product.—The decarboxylation product (0·2 g.) was dissolved in alkali (2*N*) and the calculated amount of sodium nitrite was added to the solution. The solution, thus obtained, was added to a cooled solution of 10% sulphuric acid drop by drop. The reddish precipitate was filtered, washed with cold water and crystallised repeatedly from acetic acid in red needles, m. p. 215° (decomp.). (Found in a [dry sample : N, 12·98. Calc. for $C_{10}H_8O_4N_2$: N, 12·72 per cent).

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